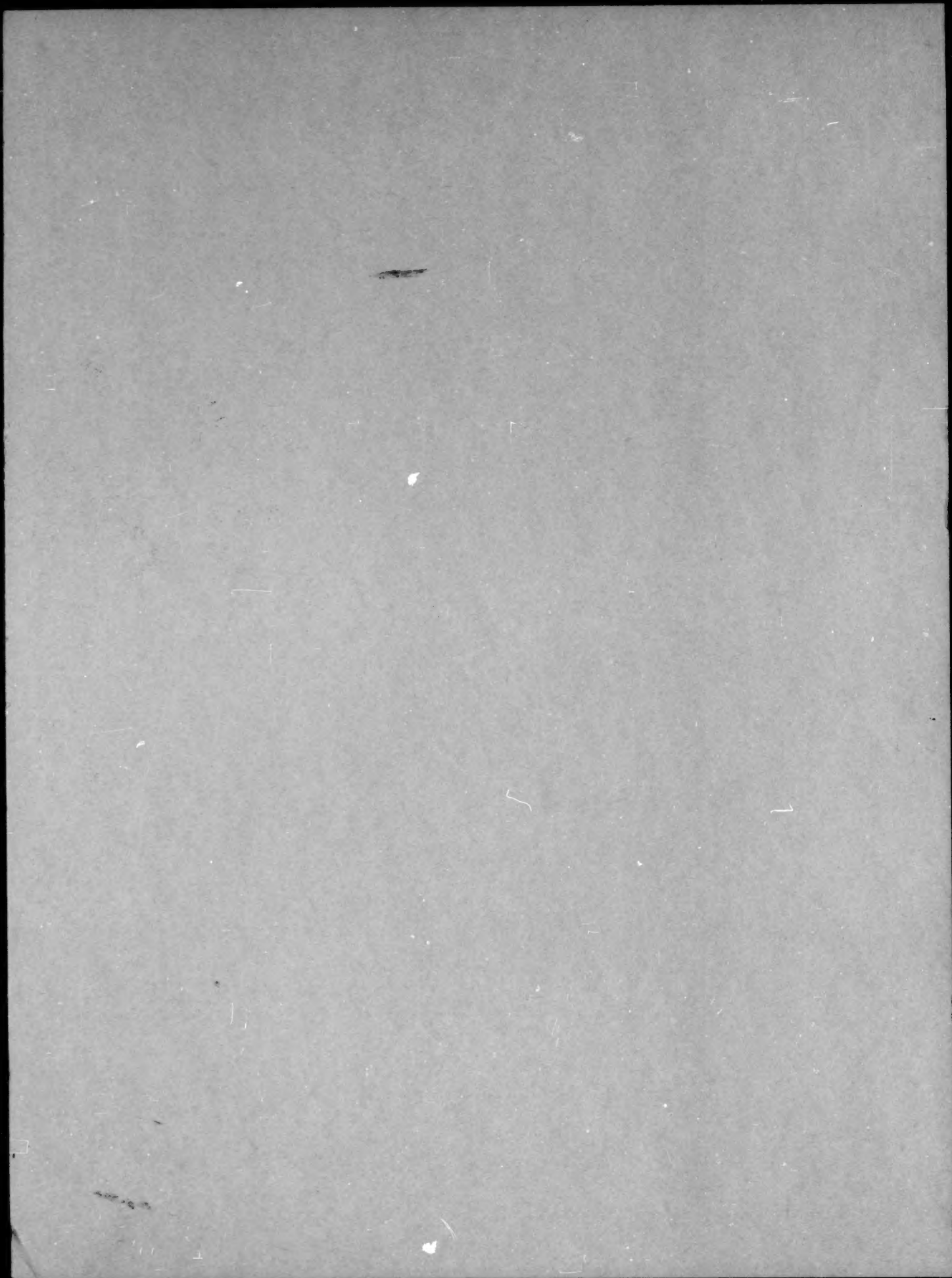


Journal of General Chemistry

Vol. 23 No. 6



SECONDARY PERIODICITY IN THE D. I. MENDELEEV TABLE OF ELEMENTS

V. P. Shishokin

In chemical texts it is usually stated that the properties of elements, arranged vertically in the D. I. Mendeleev Table, change successively. However, even in 1887, A. I. Bazarov [1] showed that a periodic change of the value of the atomic weights of elements occurs in groups of the Mendeleev Table. In order to obtain a better representation, Bazarov compared not the atomic weights, but the ratio of the atomic weights of the elements arranged side by side. Thomson showed by the determination of the heats of formation, conducted at the end of the nineteenth century and the beginning of the twentieth, that a greater affinity for oxygen was found for Cl and I, S and Te, P and Sb, than for Br, Se, and As, respectively.

The periodic changes of several properties in the groups of the Mendeleev Table were examined by E. V. Biron in 1915 in the publication, "Appearance of Secondary Periodicity" [2]. The appearance of secondary periodicity was observed in the properties of oxygen compounds (oxides, acids, and salts) of elements of the main sub-groups in groups IV-VII. In group III, the secondary periodicity is manifested less acutely, while, in groups I and II, it is scarcely apparent. Secondary periodicity is not found in the properties of hydrogen compounds.

Later, experimental investigations by Roth [3] confirmed the appearance of secondary periodicity in the change of the heats of formation of oxides in the main subgroups of groups IV-VII.

E. V. Biron's paper passed unnoticed by Russian and foreign investigators. Thus, A. M. Berkenheim [4] in his paper on the relation of the heat of formation of chemical compounds with the position of the elements in the Mendeleev Table, did not recognize the appearance of secondary periodicity, which explains the deviation of the calculated values from the experimental results.

Bazarov's paper showed the periodic change of atomic weights of elements even in the periodic table itself. The latter case is a special form of secondary periodicity subordinate to the main periodicity of the Mendeleev Table.

The present text is aimed at giving supplementary material on the periodic relationship between properties and positions of elements in the Mendeleev Table and to relate these to changes in the values of the ionization potential.

Fig. 1 gives the difference of the square roots of the eighth and first ionization potential ($\sqrt{I_8} - \sqrt{I_1}$) on the vertical axis in relation to the atomic number of the element, which is proportional to the tangent of the angle of inclination of the lines expressing Moseley's Law by means of ionization potential values (the latter are proportional to the vibration frequency). The ionization potential values are taken from Kei and Lebi's "Handbook for the Physical Investigator" [5]. The curve shows the presence of maxima for He, Ne, Ni, Pd and Pt, which corresponds to the distribution of elements in the Mendeleev Table in the following periods: H - He, Li - Ne, Na - Ni, Cu - Pd, Ag - Pt; the last period is begun by gold. The first two periods coincide with those of the Mendeleev Table, the final four do not. Therefore it must be concluded that the position of the elements in the Mendeleev Table is not immutable (this view was previously expressed by S. A. Shchukarev).

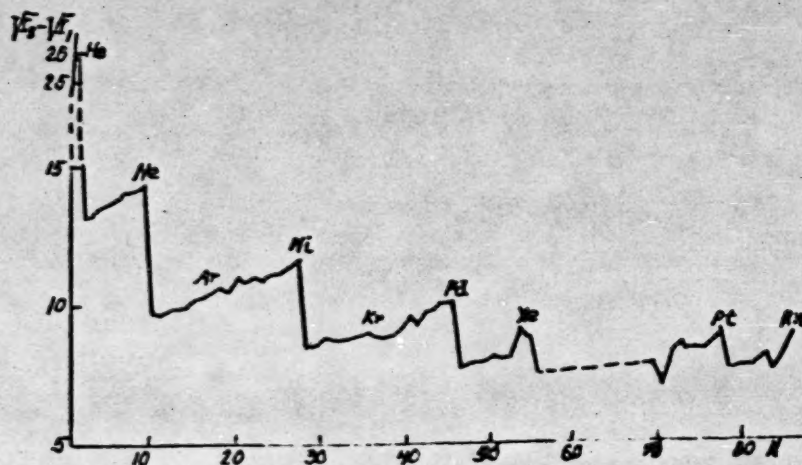


Fig. 1. Curve of the relation of the difference between the square roots of the eighth and first ionization potentials to the atomic number of the elements.

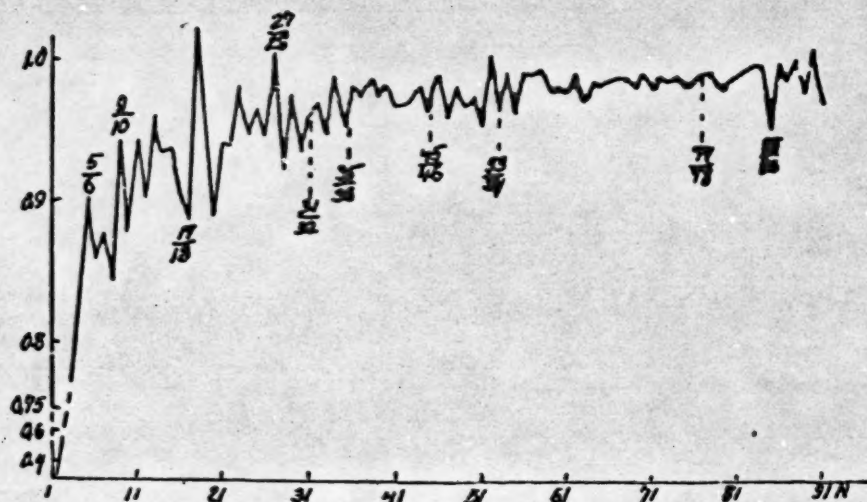


Fig. 2. Curve of the change of the ratio of the atomic weights in relation to the atomic number of the elements.

By supplementing Bazarov's diagrams with modern data which show the relation between atomic weights and atomic number of the element (in a horizontal direction on the Mendeleev Table), points corresponding to the relation of the atomic weights of gallium and germanium were of special value: up to this point, the maxima corresponded to the ratio of the atomic weights of the odd element to the even; after this point, the maxima corresponded to the ratio of the even element to the odd (Fig. 2).

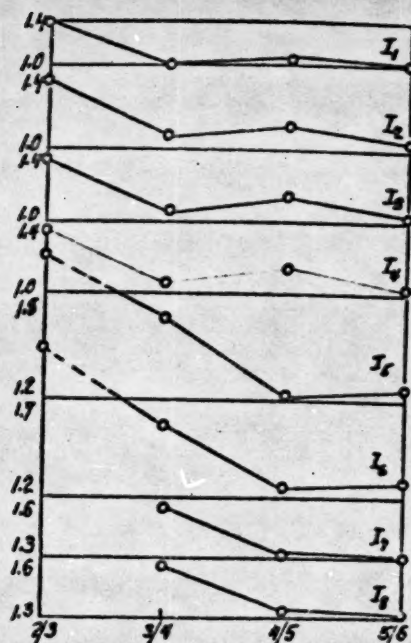


Fig. 3. Curve of the change of ionization potential for elements of the main subgroups of group IV.

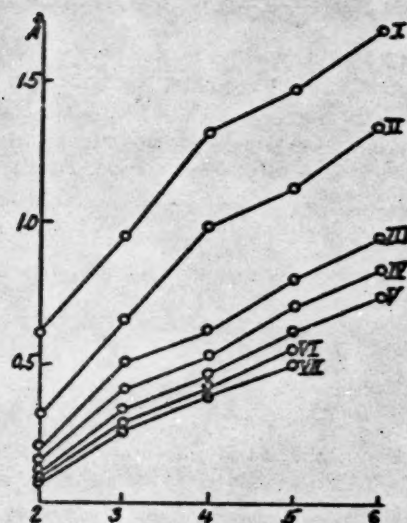


Fig. 4. Curve of the change of size of the crystals of positive ions in relation to the period number for elements of the main subgroup.

Fig. 3 gives the change of the ionization potentials (from the first to the eighth) for elements of the main subgroups of group IV, where the ratio of the ionization potential of the element (upper to the lower) is represented by the vertical axis, and the above corresponding periods by the horizontal. Periodicity is found in the change of the ionization potential only of the first second, third, and fourth potentials, i.e., it does not exceed the group number, wherein it becomes more distinct with the increase in the potential number (the periodicity is very weakly expressed for the fifth potential and is absent for the sixth, seventh and eighth). The same relationship holds for other groups of the Mendeleev Table (for the inert elements the periodicity is shown by all eight potentials; the ninth potential calculated by means of extrapolation, does not show periodicity). By placing hydrogen in group I, as well as in group VII, a periodic change of the first ionization potential occurs.

In all groups a periodic change of the atomic number (ratio of atomic numbers) of the elements of the main subgroups occurs; it appears less distinct (in gradual form) for groups III and IV. Hydrogen satisfies periodicity by being placed in group I, as well as in group VII.

In all groups except I, a distinct periodicity in the change of atomic weights (ratio of atomic weights) of elements of the main subgroups is found. In group I, the periodicity is broken only upon placing hydrogen in this group (hydrogen satisfies periodicity when placed in group VII).

The atomic volumes (ratio of atomic volumes) of the elements of the main subgroups, except for I and II, change periodically (for the zero group there is an insufficient number of results). In group I, periodicity is broken by placing hydrogen in this group, while radium causes the deviation for group II; by placing hydrogen into group VII, periodicity is satisfied.

Fig. 4 gives the change of the size of the crystalline positive ions of Pauling [6] in relation to the period num-

ber of the elements of the main subgroup. The radius of the ions in A is represented by the vertical axis, the period number, by the horizontal. In all groups with the exception of VII, a stepwise change of the radius occurs; a smooth curve is also found for group II upon transition from the second to the third period.

The heats of formation (ratio of the heats) of chlorides of the second, fourth and fifth periods show a periodic change; a smooth change occurs only in the third period. The heats of formation of halides of groups I, II, III and IV in the solid state (for group I in the gaseous state) also change periodically.

The secondary periodicity in the change of properties of elements in a vertical direction on the main subgroup of the Mendeleev Table is related, evidently, to the relative decrease in the atomic size occurring with the occupation of the d and especially, f positions by electrons. Atomic size itself determines various properties of elements, and in particular, their ionization potentials. Thus, in group IV, the silicon atom is larger than the carbon atom, and correspondingly, has a smaller value for the ionization potential. If the structure of the germanium, tin and lead atoms was analogous to that of silicon and carbon, then the total group potential (i.e., $I_1 + I_2 + I_3 + I_4$) would have been on the dotted line (Fig. 5) which is an extension of the C - Si line. However, germanium because of the inclusion of the 10 d electrons, has a structure different from silicon, which results in a considerable contraction of the germanium atom, and the latter causes an increase in the ionization potential of germanium in comparison to that of silicon. Tin has a structure analogous to that of germanium (in it 10 electrons also occupy the d position) but tin is larger, and has a correspondingly smaller value for the ionization potential. If lead, the element following tin had an analogous structure, then its ionization potential would have been on the dotted line constructed by continuing the Ge - Sn line. But lead has a different structure than tin (in it, in addition to the d position, 14 f positions are occupied by electrons) which results in a further relative contraction of the lead atom, and correspondingly, an increase of the ionization potential in comparison to that of tin.

The periodic change in the stability of oxygen compounds of the main subgroups of groups IV - VII in a vertical direction on the Mendeleev Table can be explained by the participation of a greater number of electrons in the formation of these compounds, equal to or close to the group number, and corresponding to a higher ionization potential number. Upon reaction of the elements with hydrogen, a periodic change in the vertical direction does not occur; this may be due to the fact that, during the formation of hydrogen compounds, the affinity of the elements for an electron (zero ionization potential), or a small number potential must be in effect, whereby the latter changes smoothly, or in either case, with less expression of periodicity.

SUMMARY

1. The relation between the tangents of the angle of inclination of lines expressing Moseley's Law, and the atomic number of elements is defined by a periodic curve with the following periods: H - He, Li - Ne, Na - Ni, Cu - Pd, Ag - Pt; the sixth period is begun by Au.
2. The ionization potentials of the elements of the main subgroups change periodically in the vertical direction on the Mendeleev Table in relation to the atomic number, wherein the periodicity is more expressed for potentials of higher order closest to the group number: the ionization potentials, the order of which exceeds the group number, change smoothly.
3. The periodic change, in the vertical direction, of the atomic number, atomic weight, atomic volume, and the radii of the crystalline positive ions for the main subgroups was shown.

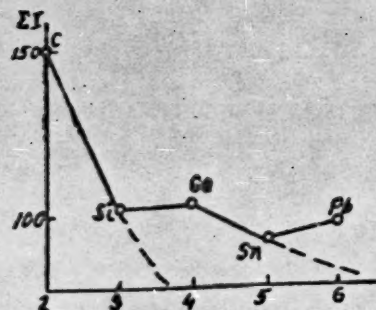


Fig. 5. Curve of the relation of the sum of the group potential to the atomic number of the elements of group IV.

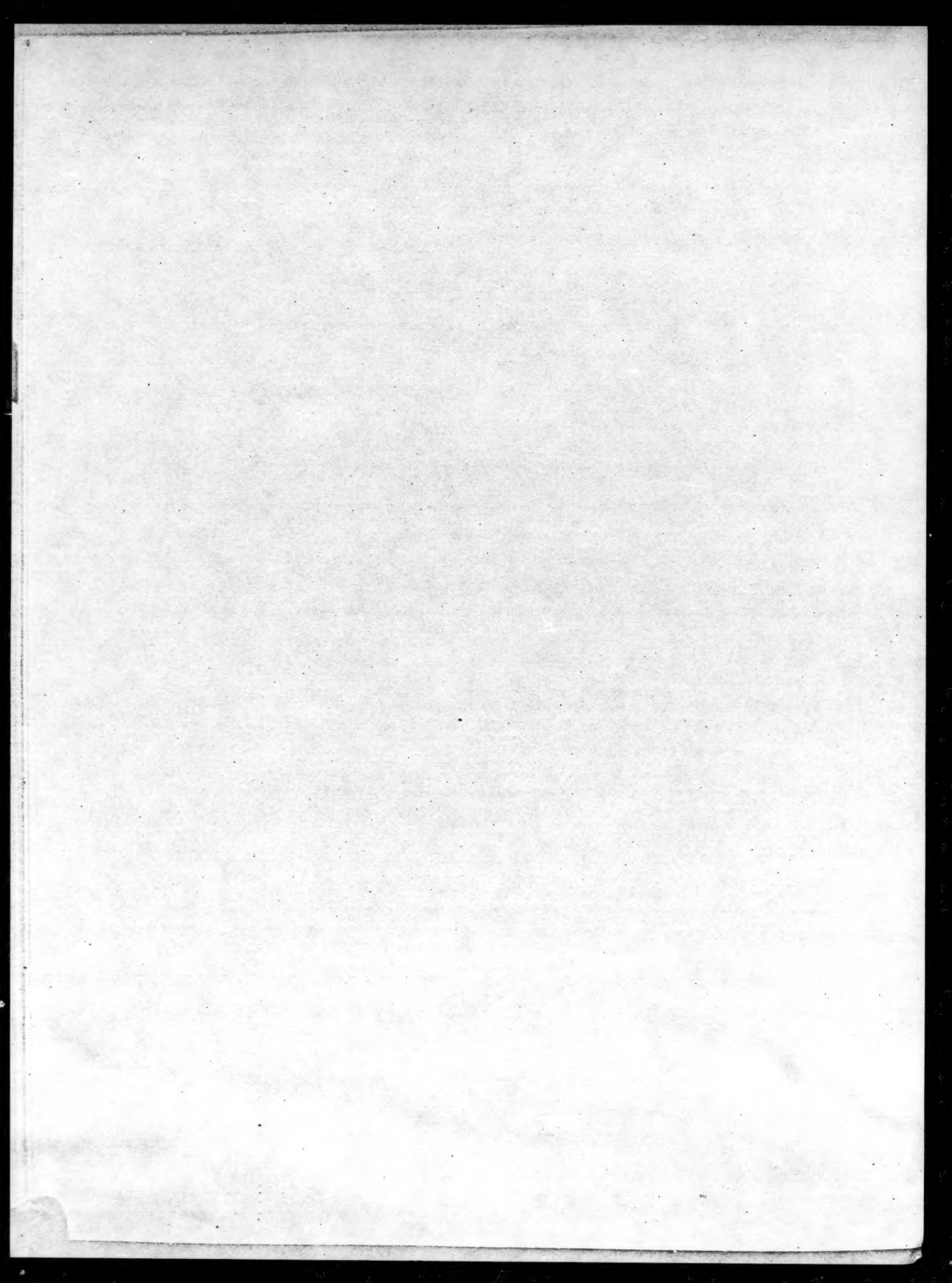
4. The periodic change of the heats of formation of chemical compounds is related to the corresponding periodic change of the ionization potentials.

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Received October 2, 1952.

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THE MUTUAL SYSTEM OF LITHIUM AND COBALT SULFATES AND CHLORIDES

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The effect of cations of the eighth group on the character of ternary mutual systems is not given in the literature because of the absence of actual examples of ternary mutual systems with the above cations participating.

The ternary mutual system studied, $\text{Li}_2\text{Cl}_2 + \text{CoSO}_4 \rightleftharpoons \text{CoCl}_2 + \text{Li}_2\text{SO}_4$, containing cations of elements of the marginal groups of the periodic table is of great interest for a more complete study of the effect of the position of elements in the periodic system on the character of ternary mutual systems.

The experimental section was conducted by the visual polythermic method with the aid of Yu. S. Butkova.

Binary systems. The binary systems $\text{CoSO}_4 - \text{Li}_2\text{SO}_4$ and $\text{Li}_2\text{Cl}_2 - \text{Li}_2\text{SO}_4$ were investigated by other authors and repeated by the authors of this communication. According to the data of Kalkanyi and Marotta [1], the system $\text{CoSO}_4 - \text{Li}_2\text{SO}_4$ had a eutectic containing 29%* of cobalt and melts at 595°. According to the author's data, the eutectic contains 27.5% of cobalt sulfate and melts at 590° (Table 1, Fig. 1).

The system $\text{Li}_2\text{Cl}_2 - \text{Li}_2\text{SO}_4$ was studied by M. Ya. Klochko [2]. According to his data, lithium chloride and sulfate form a eutectic containing 53.5% of lithium sulfate, melting at 478°. The polymorphic transformation of lithium sulfate corresponds to 572°. According to the authors' data, the eutectic contains 53% of lithium sulfate and melts at 478°. The polymorphic transformation temperature of lithium sulfate is 572°. A homeomorphic transformation is found at 564° on the fusion curve of lithium chloride (Table 2, Fig. 1).

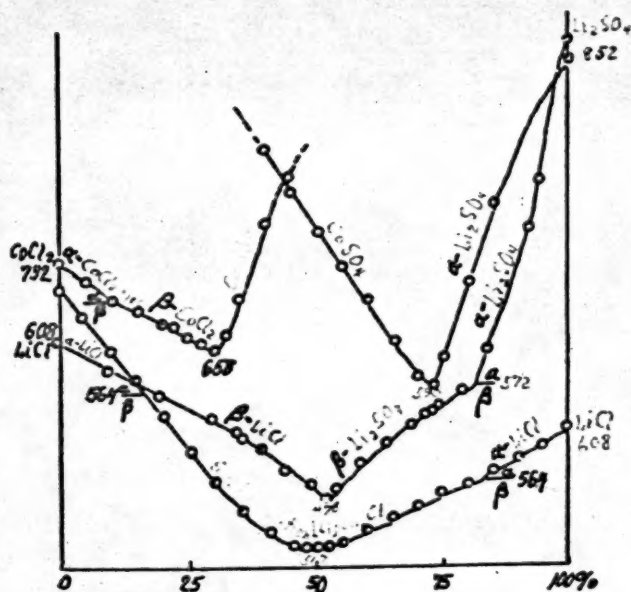


Fig. 1. Lateral sides of the squares of the mutual system.

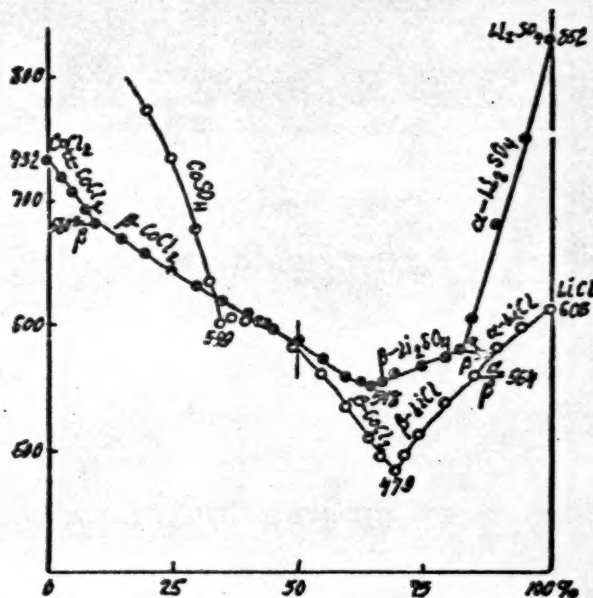


Fig. 2. Diagonal section.

* All the percents are equimolecular.

TABLE 1

Expt. No.	Equimolecular per cent		Temp. of formation of first crystals
	CoSO ₄	Li ₂ SO ₄	
1	60	40	787
2	55	45	752
3	50	50	721
4	45	55	692
5	40	60	664
6	35	65	628
7	30	70	601
8	27.5	72.5	590
9	25	75	617
10	20	80	647
11	15	85	740
12	10	90	784
13	5	95	818
14	0	100	852

The system $\text{Li}_2\text{Cl}_2 - \text{CoCl}_2$ was first studied by the authors. Lithium and cobalt chlorides form a continuous series of solid solutions with a minimum at 517° and 50% cobalt chloride. A homeomorphic transformation of lithium chloride is noted on the diagram at 565° (Table 4, Fig. 1)

TABLE 2

Expt. No.	Equimolecular per cent		Temp. of formation of first crystals	Expt. No.	Equimolecular per cent		Temp. of formation of first crystals
	Li ₂ Cl ₂	Li ₂ SO ₄			Li ₂ Cl ₂	Li ₂ SO ₄	
1	100	0	605	12	40	60	508
2	90	10	582	13	35	65	525
3	80	20	562	14	30	70	540
4	70	30	544	15	27	73	550
5	65	35	532	16	26	74	552
6	64	36	528	17	25	75	556
7	60	40	518	18	20	80	567
8	55	45	503	19	15	85	600
9	50	50	491	20	7	93	700
10	47	53	478	21	5	95	740
11	45	55	489	22	0	100	852

TABLE 3.

Expt. No.	Equimolecular per cent		Temp. of formation of first crystals	Expt. No.	Equimolecular per cent		Temp. of formation of first crystals
	CoCl ₂	CoSO ₄			CoCl ₂	CoSO ₄	
1	100	0	732	8	72	28	663
2	95	5	713	9	70	30	658
3	90	10	700	10	68	32	673
4	85	15	690	11	65	35	700
5	80	20	680	12	60	40	760
6	78	22	676	13	55	45	800
7	75	25	672				

Diagonal Sections. The stable section $\text{CoCl}_2 - \text{Li}_2\text{SO}_4$ is a binary system with a eutectic which corresponds to the composition 65% lithium sulfate and 35% of cobalt chloride at 548°. At 575° a polymorphic transformation occurs for lithium sulfate, at 680°, cobalt chloride (Table 5, Fig. 2).

The fusion curve of the unstable section $\text{Li}_2\text{Cl}_2 - \text{CoSO}_4$ consists of four branches: α, β -lithium chloride, β -cobalt chloride, and cobalt sulfate. The intersection of the branches occurs at 564° and 14%, 479° and 31%, and 479° and 31%, and 599° and 65% of cobalt sulfate, respectively. The fusion curve has a maximum at 600° and 63% cobalt sulfate (Table 6, Fig. 2).

In order to investigate the surface of the initially formed crystals of the mutual system, 15 internal sections were studied, the directions of which are shown in Fig. 3. A short characterization of each section is given in the combined table and on Figs. 4 and 5.

The results of the experimental data are summarized in the form of a projection on the square of the mutual system (Fig. 6).

The transition points on the curves of the internal sections enabled the crystallization poles to be mapped. As is apparent from Fig. 6, the mutual system consists of seven crystallization poles: cobalt sulfate, occupying 30%; α, β -lithium sulfate, 17.1%; α, β -lithium chloride, 18.1%; α, β -cobalt chloride, 34.8% of the total area of the square.

The stable diagonal section cobalt chloride - lithium sulfate separates the square of the mutual system into two ternary systems: $\text{CoCl}_2 - \text{Li}_2\text{SO}_4 - \text{Li}_2\text{Cl}_2$ with a ternary eutectic E_1 of the composition: 44% lithium chloride, 36% lithium sulfate, 20% of cobalt chloride, melting at 452°, and $\text{CoCl}_2 - \text{Li}_2\text{SO}_4 - \text{CoSO}_4$ with a ternary eutectic

Combination Table

Section No.	Starting mixture of the components	M. p. of starting mixture	Component added	Branches of the crystallization curves and their intersections								Maxima on the curves		Fig. no.							
				Branch I	Inter-section of I and II	Branch II	Inter-section of II and III	Branch III	Inter-section of III and IV	Branch IV											
													%		t°	%	t°	%	t°	%	t°
I	80% CoCl ₂ + 20% CoSO ₄	679	Li ₂ SO ₄	β-CoCl ₂	63.530	β-Li ₂ SO ₄	81.573	α-Li ₂ SO ₄						4							
II	45% Li ₂ SO ₄ + 55% CoSO ₄	752	Li ₂ Cl ₂	CoSO ₄	17.510	β-Li ₂ SO ₄ + β-CoCl ₂	60.477	β-LiCl	85.564	α-LiCl	35.543			4							
III	55% Li ₂ SO ₄ + 45% CoSO ₄	690	Li ₂ Cl ₂	CoSO ₄	13.530	β-Li ₂ SO ₄								4							
IV	65% Li ₂ SO ₄ + 35% CoSO ₄	625	Li ₂ Cl ₂	CoSO ₄	7.551	β-Li ₂ SO ₄	55.470	β-LiCl			27.562			4							
V	70% Li ₂ SO ₄ + 30% Li ₂ Cl ₂	540	CoSO ₄	β-Li ₂ SO ₄	46.507	CoSO ₄					22.566			4							
VI	50% Li ₂ SO ₄ + 50% Li ₂ Cl ₂	494	CoSO ₄	β-LiCl	2.475	β-Li ₂ SO ₄	40.531	β-CoCl ₂	52.549	CoSO ₄	32.554			4							
VII	30% Li ₂ SO ₄ + 70% Li ₂ Cl ₂	546	CoSO ₄	β-LiCl	21.452	β-CoCl ₂	58.572	CoSO ₄			55.574			4							
VIII	25% Li ₂ SO ₄ + 75% Li ₂ Cl ₂	557	CoCl ₂	β-LiCl	43.490	α-CoCl ₂								5							
IX	5% Li ₂ SO ₄ + 95% Li ₂ Cl ₂	—	CoCl ₂	β-LiCl	48.494	α-CoCl ₂								5							
X	75% Li ₂ Cl ₂ + 25% CoCl ₂	562	CoSO ₄	β-LiCl	21.5484	β-CoCl ₂	60.609	CoSO ₄			55.615			5							
XI	63% Li ₂ Cl ₂ + 37% CoCl ₂	531	CoSO ₄	β-LiCl	10.488	α-CoCl ₂								5							
XII	50% Li ₂ Cl ₂ + 50% CoCl ₂	511	CoSO ₄	α-CoCl ₂	15.545	β-CoCl ₂	55.621	CoSO ₄			47.624			5							
XIII	40% Li ₂ Cl ₂ + 60% CoCl ₂	—	Li ₂ SO ₄	β-CoCl ₂	52.5520	β-Li ₂ SO ₄	80.575	α-Li ₂ SO ₄						5							
XIV	38% Li ₂ Cl ₂ + 62% CoCl ₂	538	CoSO ₄	α-CoCl ₂	12.568	β-CoCl ₂								5							
XV	25% Li ₂ Cl ₂ + 75% CoCl ₂	607	CoSO ₄	α-CoCl ₂	9.25	β-CoCl ₂	43.643	CoSO ₄			25.662			5							

TABLE 4

Experiment No.	Equimolecular %		Temp. of formation of first crystals	Experiment No.	Equimolecular %		Temp. of formation of first crystals
	CoCl ₂	Li ₂ Cl ₂			CoCl ₂	Li ₂ Cl ₂	
1	100	0	732	13	47	53	519
2	95	5	707	14	45	55	522
3	90	10	680	15	40	60	530
4	85	15	656	16	35	65	539
5	80	20	628	17	30	70	548
6	75	25	600	18	25	75	557
7	70	30	572	19	20	80	565
8	65	35	549	20	15	85	575
9	60	40	532	21	10	90	585
10	55	45	521	22	5	95	595
11	52	48	518	23	0	100	608
12	50	50	517				

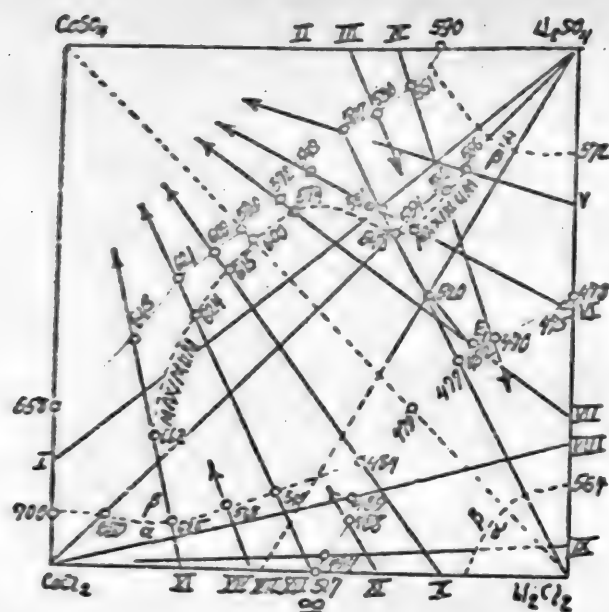


Fig. 3. Directions of the internal sections.

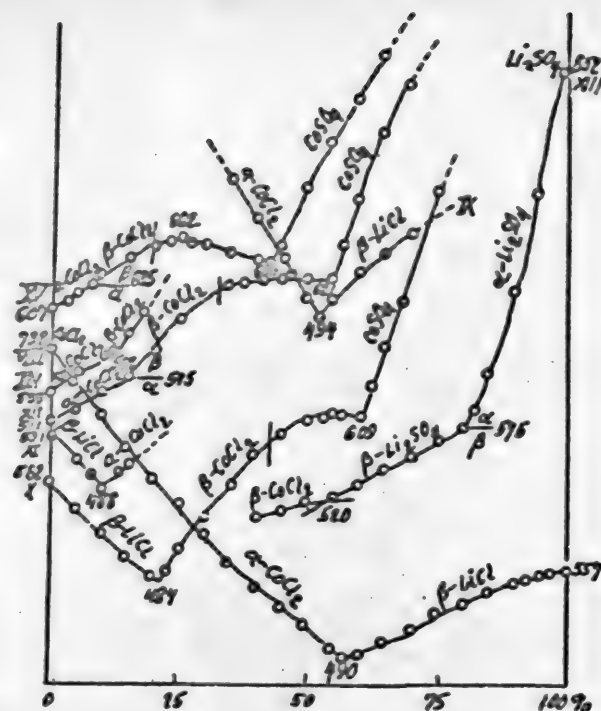


Fig. 5. Internal sections VIII - XV.

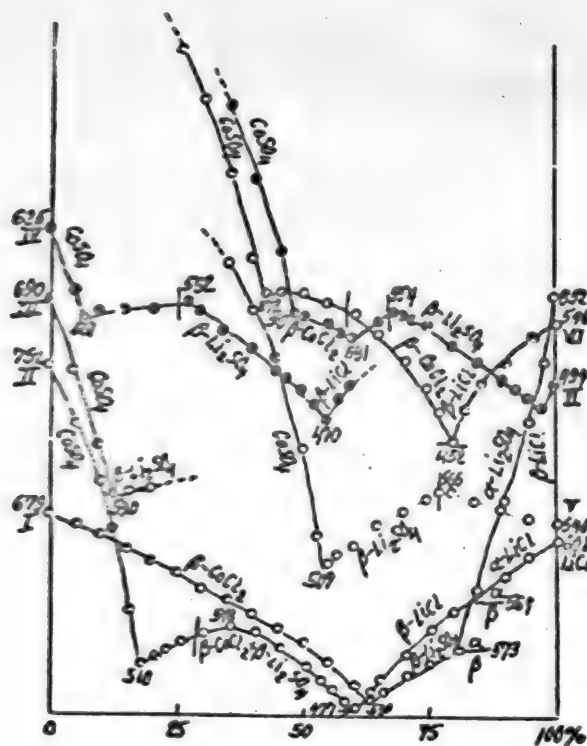


Fig. 4. External sections I - VII.

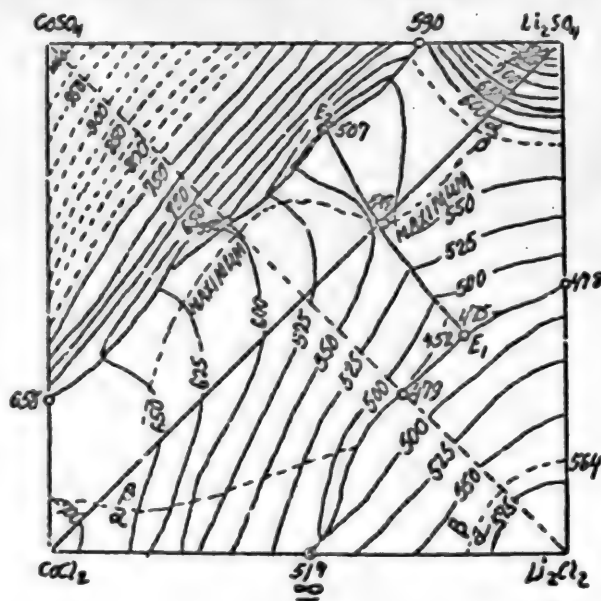


Fig. 6. Projection of the isotherms on the composition square.

TABLE 5

Experiment No.	Equimolecular %		Temp. of formation of first crystals
	CoCl ₂	Li ₂ SO ₄	
1	100	0	732
2	97	3	716
3	95	5	703
4	92	8	692
5	90	10	680
6	85	15	668
7	80	20	654
8	75	25	641
9	70	30	628
10	65	35	615
11	60	40	605
12	55	45	595
13	50	50	582
14	45	55	570
15	40	60	557
16	37	63	550
17	35	65	548
18	33	67	553
19	30	70	557
20	25	75	564
21	20	80	571
22	18	82	575
23	15	85	600
24	10	90	674
25	5	95	746
26	0	100	852

TABLE 6

Experiment No.	Equimolecular %		Temp. of formation of first crystals
	Li-Cl	CoSO ₄	
1	100	0	608
2	95	5	593
3	90	10	577
4	85	15	562
5	80	20	533
6	75	25	508
7	72	28	494
8	70	30	481
9	67	33	494
10	65	35	503
11	60	40	530
12	55	45	556
13	50	50	581
14	45	55	594
15	43	57	597
16	40	60	599
17	37	63	600
18	35	65	599
19	33	67	628
20	30	70	672
21	25	75	730
22	20	80	770

E₂ of the composition: 30% lithium sulfate, 54% cobalt chloride, and 16% cobalt sulfate, melting at 507°. The continuous solid solutions with a minimum at 517° which are formed in the system of cobalt and

lithium chlorides, are destroyed by the addition of a small amount of the third component.

In order to make the melting points and the positions of the invariant points, as well as the common crystallization curves of the components more accurate, projections of the above points and curves of the square on the sides CoCl₂-Li₂Cl₂ and Li₂Cl₂-Li₂SO₄ were made.

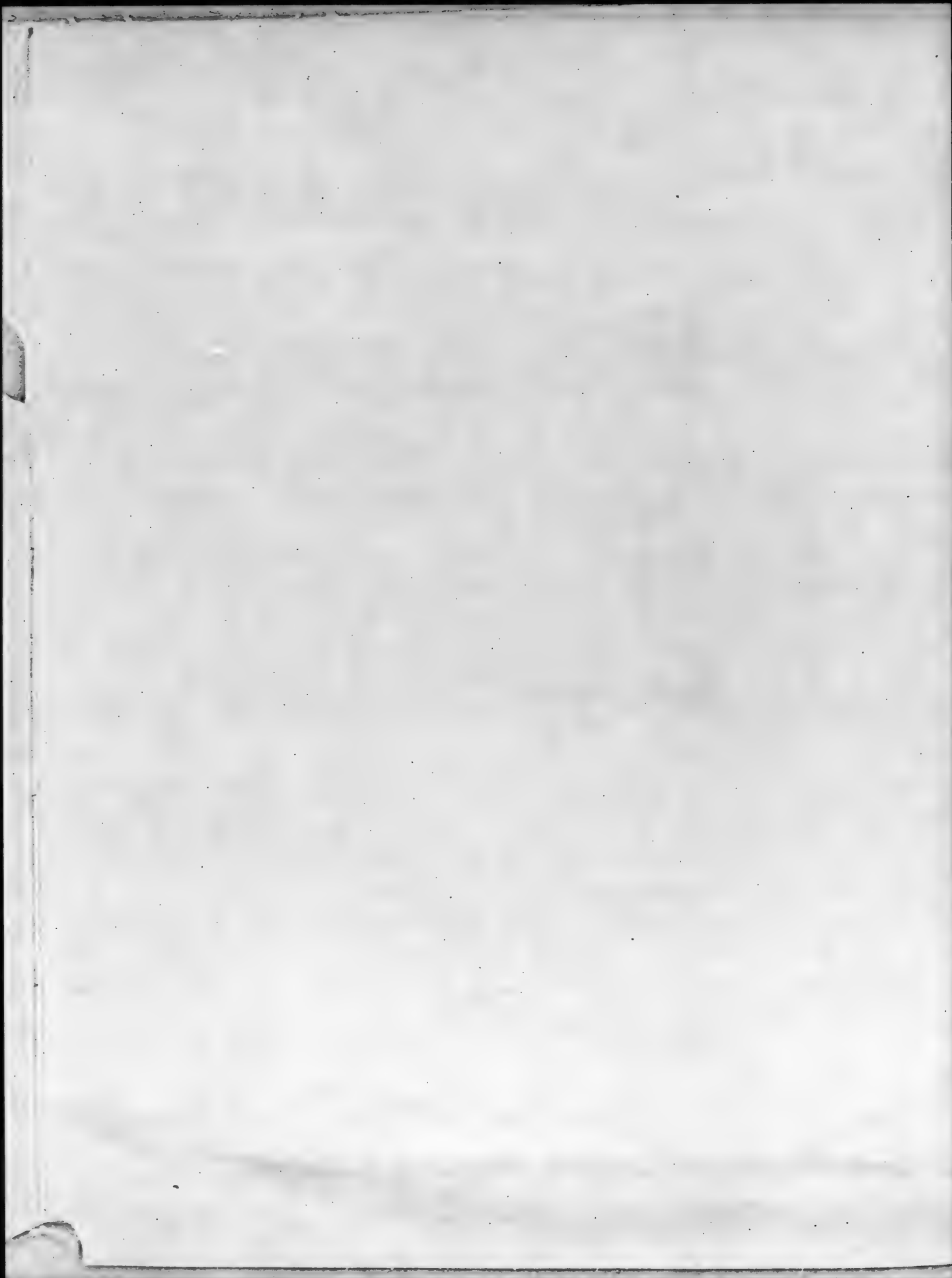
SUMMARY

1. The system of lithium and cobalt chlorides and sulfates was first studied by the visual-polythermic method of physico-chemical analysis, and was assigned to the irreversible-mutual systems by its thermochemical effect, as well as by its character. But the deviation of the ridge in the pole cobalt chloride and lithium sulfate from the plane of the stable diagonal section is an indication of some reversibility of the exchange reaction.
2. The reaction is directed toward the stable pairs: cobalt chloride-lithium sulfate, which agrees with the thermochemical effect of the exchange reaction, equal to 6.82 kcal per equivalent.
3. The stable diagonal section of cobalt chloride and lithium sulfate separates the ternary mutual system into two ternary systems: CoCl₂-Li₂SO₄-Li₂Cl₂ with the ternary eutectic at 452° and CoCl₂-Li₂SO₄-CoSO₄ also with a ternary eutectic point, at 507°.
4. The solid solution with a minimum at 517° and 50% lithium chloride, which is formed in the lateral binary system of cobalt and lithium chloride, is destroyed within the mutual system by the addition of small amounts of the other components.

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STRUCTURE OF COBALTIC AND NICKEL HYDROXIDE PRECIPITATES

S. I. Sobol

Cobaltic hydroxide, $\text{Co}(\text{OH})_3$, is usually prepared by the oxidation of a cobaltous chloride or sulfate solution in neutral or weakly acidic medium with strong oxidizing agents (hypochlorite, persulfate, electric current, etc.). The precipitate contains varying amounts of zeolytic water in relation to the conditions of preparation, which are removed by heating over 100° .

Different authors assign various structures to the precipitate. In earlier investigations [1], $\text{Co}(\text{OH})_3$ was assigned a crystalline structure; however, LeBlank and Muller [2] could not detect a crystal lattice in the hydroxide Co_2O_3 , precipitated from solution by means of X-rays, while Co_2O_3 obtained by a dry method (fusion) shows it readily. For this reason [2], they considered that cobaltic hydroxide has a disordered spatial lattice and cannot be considered a crystalline substance. In order finally to solve this problem of the structure of cobaltic hydroxide precipitate, it was necessary to investigate it by many methods. The structure of the precipitate of $\text{Co}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ formed by hypochlorite from chloride and sulfate solutions having a pH 1.5 - 2.0 and at 20 to 80° were investigated.

The investigations were conducted in transmitted and polarized light at small magnifications, as well as with the aid of an electron microscope; electronograms were taken for a preparation deposited on a collodion film at magnifications up to 9000 times.

For visual investigations and photography in visual and polarized light, drops of freshly precipitated pulp were placed on a glass slide and covered with a cover glass.

All operations with such preparations were conducted within a short time, maximum 1-2 hours, and thus were protected from all sorts of distortions possibly arising during drying of the precipitate, as for example crystallization of salts from the mother liquor.

Investigation of cobaltic hydroxide precipitates in non-polarized light showed the following:

1. In mass, the particles of the residue obtained at the same rate of addition of hypochlorite from sulfate solutions, as well as from hot solutions, are considerably coarser than those obtained from chlorides, as well as from cold solutions (Figs. 1 - 3).
2. Particles of the residue always have an uneven form; the borders of the particles are sometimes folded.
3. Fine and medium particles are translucent and are colored yellow; the coarse are opaque and are colored only at the borders; in large mass (on the filter, or in the pulp) cobaltic hydroxide precipitates have a dark brown or sometimes a black color.
4. An examination of the precipitate removed from the pulp at the time of the precipitations of the cobalt with sodium hypochlorite at 80° from an acidified starting solution ($\text{pH} \approx 1.9$) showed that the color of the particles changes sharply when the pH of the medium became 2.3 - 2.5; even fine, translucent, yellow particles gradually lost translucency and became dark brown, almost black; upon chemical analysis, this residue showed that the cobalt in it was oxidized to more than trivalency.
5. Decrease of the rate of addition of hypochlorite to the solution, all other conditions being equal, led to the preparation of a coarser, on the average, precipitate. However, no amount of slowing down of the precipitation of cobaltic hydroxide could lead to the preparation of particles with a noticeable crystal lattice.

Upon examination of particles of the precipitate in transmitted polarized light, and upon rotation of the objective, the particles disappeared from the field of vision, a phenomenon characteristic for non-crystalline substances.

The electronograms of the finer particles of cobaltic hydroxide are shown in Figs. 4 - 9, which were precipitated from a chloride solution at 80° and pH 1.5, and they very graphically show the absence of crystalline structure

See plate, page 1115.

in the particles of the precipitate.

It is apparent from the photographs that the finest particles of the hydroxide, which have a cross section of tenths of a micron, were fused together to form aggregates of various coarseness. Therefore, coarse particles of $\text{Co}(\text{OH})_2$ are formed by the coagulation of particles of colloidal size, i.e., particles of the cobaltic hydroxide visible to the eye or at slight magnifications with the visual microscope are gels, not crystals.

Because coarse particles are formed by the combination of a large number of very small ones having an irregular form, the coarse particles must be viewed as not being monolithic, but as friable aggregates. Electronic rays gave only the shape of such aggregates (shown in Figs 7 and 8*) because these figures do not show any monolithic structure in coarse particles.

During the process of combination of the particles, micro-volumes filled with mother liquor remain isolated from the surface within the coarse aggregates being formed; special experiments showed that substances present in the mother liquor, which are not coprecipitable with cobaltic hydroxide, are not removed from the particles of the precipitate even with thorough and continued repulping. However, these impurities are to a great extent (80-84%) removed from an initially repulped wet precipitate of cobaltic hydroxide by pressing the latter under a pressure of 80-100 kg/cm². These experiments served as important proof of the porosity of coarse cobaltic hydroxide particles and supplemented the information on the structure of the latter obtained by other methods of investigation.

Higher nickel hydroxides obtained by various methods are not in a chemical sense, homogenous substances; most probably they are solid solutions of $\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_3$ of varying composition [3].

The structure of these precipitates was more than once the subject of an investigation. X-ray investigations [2] of the higher nickel hydroxides showed that they were so greatly dispersed that, after a 3-day drying at 100°, no trace of any crystal lattice could be seen on the X-raygrams.

The higher nickel hydroxides were investigated only with ordinary transmitted light at magnifications up to 160 times. The nickel precipitates were translucent, dark brown, flocculant particles of irregular form, disappearing from the field of view upon examination with polarized light and rotation of the objective. With increase in temperature, the coarseness of the particles increased (Figs 10 and 11*); increase of the pH of the medium had the same effect. Fig 12* shows the initial stage of formation of coarse aggregates by the combination of fine particles occurring during the precipitation with neutral sodium hypochlorite from a nickel sulfate having a pH 3.96 and at 80°.

Visual observation with a binocular microscope of samples of the pulp removed during the process of precipitation over short intervals of time, showed that the fine particles, formed initially, combined rapidly after the addition of sodium hypochlorite portion ended, and after 3-5 minutes, large friable aggregates were formed in the pulp (Fig. 13*). By changing the focus of the microscope, the many internal spaces in such primary aggregates could be seen. However, because of the great size of these aggregates, when one of these is found in focus, the other leaves it, and sometimes it appears to be monolithic.

After many minutes, sometimes hours, the primary friable aggregates have time to condense considerably; this process which is observed to proceed with time, is aided by a slight stirring of the pulp at higher temperatures. It is interesting that, in contrast to particles of nickel hydroxides, those of cobaltic hydroxide precipitated at low temperatures, do not grow as coarse upon further heating and mixing of the pulp. Fig. 13* shows such condensed aggregates.

It is interesting to point out that, in contrast to nickel precipitates, it was possible to observe and find separate stages in the growth of coarseness of cobaltic hydroxide particles only with the use of much higher magnifications; the particles of nickel hydroxide are themselves considerably coarser.

Therefore, it can be considered confirmed that particles of cobaltic hydroxide and higher nickel hydroxides do not have a noticeable crystalline lattice and must be viewed as gels.

Upon the precipitation of ferric hydroxide, a close analog of cobalt and nickel in the periodic system, in relation to the temperature conditions and rate of precipitation, residues in amorphous gel like state, as well as in clearly expressed crystalline form, can be obtained. In the case of the precipitation of trivalent cobalt and tetravalent nickel hydroxides, no sort of deceleration of precipitation results in the formation of an obviously crystalline precipitate. The reason for this must be sought in the various properties of Fe^{III} , Co^{III} , and Ni^{IV} . Fe^{III} is very stable in aqueous solution and in the presence of certain other ions, as for example the chloride ion. This is

See Plate, page 1115.

the result of the small relative value of the redox potential of the pair $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ (0.77 V). Co^{III} and, especially Ni^{IV} , in such solutions, and especially at higher temperatures, are very unstable, since according to the value of the redox potential ($\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ 1.82V, while for $\text{Ni}(\text{OH})_2\text{-Ni}^{\text{II}}$ 2.0 V[3]), they can not only oxidize Cl^- ion atomic chlorine, but the hydroxyl ion (with the evolution of oxygen), as a result of which the concentration of Co^{III} and Ni^{IV} , within a short time (seconds and fraction of seconds), falls to an insignificant value approaching the equilibrium defined by the solubility product of the corresponding solid phase.

On the strength of this phenomenon, conditions for the hydrolysis of salts of Co^{III} and Ni^{IV} are radically different from those for the hydrolysis of Fe^{III} salts, namely, the necessary time and material is lacking for the formation of a crystal lattice of cobaltic hydroxide and the higher nickel hydroxides, and the primary particles of these hydroxides formed in very dilute (for Co^{III} and Ni^{IV}) solutions naturally cannot have coarse sizes. The formation of primary particles of the precipitate of $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ can only occur at the time of the introduction of some strong oxidizing agent; after it is no longer available in the solution, almost at once the formation of primary particles of the precipitate stops. The gel like particles of the precipitate, possessing an enormous surface energy, tend to decrease the store of the latter by combining (coagulation) into coarse particles.

SUMMARY

1. Cobaltic and higher nickel hydroxide precipitates were subjected to microscopic investigation in transmitted and polarized light; in addition, the cobaltic hydroxide precipitates were investigated by means of the electron microscope.
2. It was found that coarse cobaltic and nickel hydroxide particles do not have a crystalline structure and are formed by coagulation of particles of colloidal size; therefore, these hydroxides are gels.
3. A suggestion was made as to the reasons why cobaltic and higher nickel hydroxides did not form a crystal lattice during the process of precipitation.

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Received December 8, 1952

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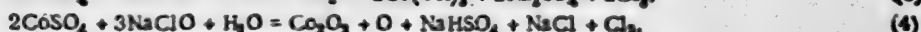


PHYSICO-CHEMICAL CONDITIONS OF PRECIPITATION, HEAT OF FORMATION AND SOLUBILITY PRODUCT OF COBALT HYDROXIDE

S. I. Sobol

Cobaltic hydroxide is usually prepared by the oxidation of cobaltous salts in heated neutral or weakly acidic solution by some strong oxidizing agent, sodium, potassium, and calcium hypochlorite, gaseous chlorine, ozone, persulfate, or an electrical current [1, 2, 3, 4]. However, literature reports on the physico-chemical conditions and chemism of the precipitation of cobalt hydroxide are very scarce and contradictory, while the heat of formation and solubility product have only one result which must be viewed as an approximate one.

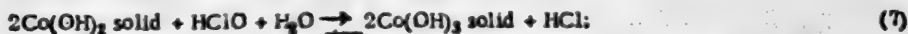
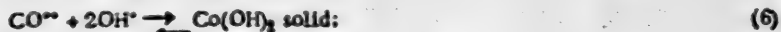
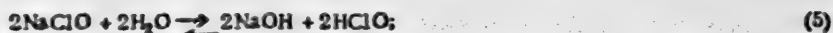
Certain authors [1, 2, 3, 4, 5, 6] describe the oxidation-precipitation of cobalt by hypochlorite in this form:



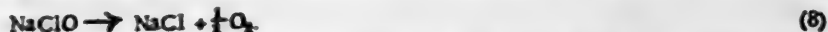
combining in one equation, apart from the basic reaction, a series of parallel side reactions which proceed with the evolution of chlorine and oxygen.

These authors do not formulate a viewpoint on the question of the mechanism of the process of oxidation-precipitation of cobalt. Other authors [7, 8] start from the assumption that the chemical oxidant was not strong enough to guarantee the oxidation of the Co^{2+} to the Co^{3+} in the solution as the first stage of the reaction (1) - (4), because the redox potential of the process $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ is very great. For this reason the second group of authors believe that the first stage must necessarily be the precipitation of the hydrated cobalt oxide, and the second, the oxidation of $\text{Co}(\text{OH})_2$ by the hypochlorite, chlorine, or some other chemical oxidizer to $\text{Co}(\text{OH})_3$.

Drexel, for example, gives the following order for the reaction for the case of the application of a neutral solution of hypochlorite:



the excess hypochlorite, consisting of 50% for the above, is catalytically decomposed by the cobalt hydroxide.



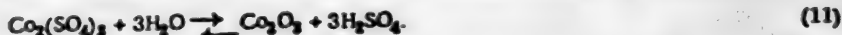
Bray [8] cites (7) for the case of the application of hypochlorite and reaction (9) for gaseous chlorine.



Only the application of a very active oxidizing agent as an electrical current, is able, according to Drexel, to cause the oxidation of cobalt on the anode (as the first stage of the process), if the electrolysis is conducted in dilute sulfuric acid



the hydroxide appears in the second stage of the process as a result of the hydrolysis of the cobalt oxy sulfate



Drexel recommends that the precipitation of cobaltic hydroxide be done at pH 2.5-2.8 with hypochlorite;

Chufarov and co-workers [9] found that at room temperature, cobaltic hydroxide is formed in solutions of chlorides by the action of hypochlorous acid at pH 3.0-3.2, in solutions of sulfates, at pH 4.4-6.0.

The authors' results indicate that hypochlorous acid and gaseous chlorine cause the precipitation of cobalt hydroxide from much more acidic solution having a pH which sometimes is less than unity. Here the formation of cobaltous hydroxide, as the first stage of the formation of cobaltic hydroxide, is absolutely excluded since it is known [10, 11] that the precipitation of $\text{Co}(\text{OH})_2$ requires a considerably higher pH (of the order of 6-7).

The relative activity of the cobalt ions of different valency in the solution corresponding to activity of the oxidizing agent used, is determined by the Nernst equation

$$E = E_0 \frac{\text{Co}^{2+}/\text{Co}^{3+}}{+ \frac{RT}{nF} \ln \frac{a_{\text{Co}^{3+}}}{a_{\text{Co}^{2+}}}} \quad (12)$$

where the activity of Co^{3+} is independently related to the activity product of cobaltic hydroxide.

$$L_{\text{Co}(\text{OH})_3} = a_{\text{Co}^{3+}} \cdot a_{\text{OH}^-}^3 \quad (13)$$

If it is considered that the activity of OH^- is defined by the ion product of water

$$K_w = a_{\text{H}^+} \cdot a_{\text{OH}^-} \quad (14)$$

and that, by definition, $-\log a_{\text{H}^+} = \text{pH}$ (15), substituting the corresponding values into (12), and transposing to logarithms to the base ten, we obtain:

$$E = E_0 \frac{\text{Co}^{2+}/\text{Co}^{3+}}{+ bT (\log L_{\text{Co}(\text{OH})_3} - 3 \log K_w - 3\text{pH} - \log a_{\text{Co}^{2+}})} \quad (16)$$

Equation (16) expresses the relationship of the process of the oxidation of $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ and the subsequent hydrolysis of the Co^{3+} salts, relating the important parameters, temperature, pH of the solution, activity of the bivalent cobalt ions, with the physico-chemical properties of the oxidizing agent (by means of the values of the true redox potential E).

Analysis of equation (16) shows that, if the representation of the consecutiveness of the separate stages of the process of preparation of cobaltic hydroxide (first the oxidation of Co^{2+} into Co^{3+} , then the hydrolysis of the Co^{3+} salts), which was the basis of its derivation, is correct, then, during the precipitation of the hydroxide at constant temperature, the following relationships must be found: based on the oxidation and precipitation of the cobalt in the form of cobaltic hydroxide, i.e. based on the decrease in the active concentration of the bivalent cobalt, the pH of the solution must gradually increase; the stronger the oxidizing agent used, i.e., the higher the value of the redox potential (E), the smaller will the equilibrium pH of the solution be at the given active concentration of cobaltous oxide.

Nothing can be said beforehand about the effect of the increase in temperature of the solution on the direction of the transposition of the curves of change of equilibrium pH during the oxidation-precipitation of cobalt; E can increase or decrease in relation to the properties of the oxidizing agent and with increase in temperature, which introduces some uncertainty into the relation between the constant (at the given temperature) coefficients of equation (16). This question can be answered experimentally in each particular case.

The heat of formation of cobaltic hydroxide had been measured by Thomson in 1882-1886. Thomson measured the heat of the reaction:



in a calorimeter.

Britke and Kapustinsky [12] calculated the heat content of $\text{Co}(\text{OH})_3$ at 18° to be equal to 177,000 cal/mole for formation from the elements) from his data.

Almost forty years after Thomson's investigation, it was shown during an investigation of (17) proceeding in neutral medium [6] that the thin surface layer of particles of the precipitate was oxidized to cobalt peroxide which very actively decomposed the hypochlorite catalytically, which then could enter into the main reaction. The amount of decomposed hypochlorite is almost undeterminable and depends on many small factors (rate of addition of the hypochlorite into the solution, efficiency of stirring of the pulp, etc.); for this reason it can be supposed that less than

the corresponding stoichiometric amount of hypochlorite participated in reaction (17) in Thomson's experiments. On the other hand, the amount of alkali used was always sufficient for the complete precipitation of the cobalt in the form of cobaltous hydroxide $\text{Co}(\text{OH})_2$, and for this reason, a certain (undeterminable) part of the latter must have been always unoxidized.

In view of the above data which, it must be thought, were unknown to Thomson, it must be recognized that the method chosen by him for the determination of the heat of formation of $\text{Co}(\text{OH})_2$ was not applicable, and in principle, could not give correct results. However, no one, after Thomson, used other physico-chemical methods for the determination of ΔH .

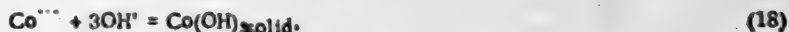
It must also be mentioned that Thomson considered cobaltic hydroxide crystalline; later investigators showed that $[\text{Co}(\text{OH})_2 \cdot x\text{H}_2\text{O}]$ does not have a noticeably expressed spatial lattice and is a gel.

The solubility product of cobaltic hydroxide was calculated at 25° by Latimer [15]; starting from the value of the heat of formation (-173,000 cal/mole) obtained by Thomson, and an approximate accepted entropy of formation of 103.2 cal/degree, Latimer obtained the free energy of formation of $\text{Co}(\text{OH})_2$ from the elements, -142,000 cal/mole, from which $L = 2.5 \cdot 10^{-43}$. Because of the uncertainty of the results of Thomson's experiments, used by Latimer as the basis for the calculation of the solubility product, the value of the latter (according to Latimer) must only be accepted as a first approximation. Undoubtedly in any case, cobaltic hydroxide is a very poorly soluble compound.

The solubility of the hydroxide, equal to $5.6 \cdot 10^{-8}$ mg/liter or about 10^{-7} g-ions of Co^{+++} per l., was found with the aid of the radioactive isomer of cobalt [16]. There was no possibility of examining the original paper [16] and the conditions under which this value was obtained (pH, temperature, and others) is not known.

Considering all of the above on the question of the determination of the heat of formation and solubility product of $\text{Co}(\text{OH})_2$, it was necessary to once more determine these constants using a method which excluded the above errors.

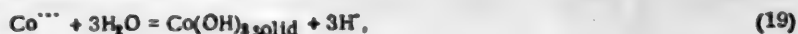
For this reason, the equilibrium constant of the hydrolysis reaction of Co^{+++} was determined (for several temperatures in the interval 19-81°)



from which

$$K' = \frac{1}{a_{\text{Co}^{+++}} a_{\text{OH}^-}^3} \quad (18')$$

which is identical (in a thermodynamic sense) with the reaction



from which

$$K' = \frac{a_{\text{H}^+}^3}{a_{\text{Co}^{+++}}} \quad (19')$$

reaction (19) more accurately describes the chemism of the hydrolysis of the salts of Co^{+++} in an acidic medium.

From (19') we obtain

$$\log K' = -3\text{pH} - \log a_{\text{Co}^{+++}} \quad (20)$$

which makes it possible to apply the known equation

$$\log \frac{K_2}{K_1} = -\frac{Q_1(T_2 - T_1)}{4.575 T_1 T_2} \quad (21)$$

to find Q_1 , the heat effect of the reaction of formation of $\text{Co}(\text{OH})_2$ from the ions Co^{+++} and OH^- , since the heats of formation of: Co^{+++} from Co [12] equal to +16500 cal/g-ion, Co^{++} from Co^{+++} [17] equal to +33700 cal/g-ion, (thus the heat of formation of Co^{++} from elementary cobalt in solution is +50200 cal/g-ion, and OH^- from the elements [12], equal to 54660 cal/g-ion, is known from the literature, then there is no difficulty in calculating Q_1 , the heat of formation of cobaltic hydroxide from the elements.

Using the values of $a_{\text{Co}^{+++}}$ and a_{OH^-} found experimentally, is also easy to determine the activity product of cobaltic hydroxide, L_2 (13).

EXPERIMENTAL

The precipitation of cobaltic hydroxide was effected by sodium hypochlorite solution from solutions of CoSO_4 and CoCl_2 . The solution in a flask was efficiently stirred, and the hypochlorite was added dropwise from a burette. The true redox potential generated in the solution was measured by means of the usual compensation scheme by smooth platinum electrode versus a saturated calomel one. The flask with solution was placed into an aqueous thermostat the temperature of which was held with an accuracy of $\pm 0.5^\circ$.

TABLE 1

Change in Parameters During the Precipitation of Cobaltic Hydroxide from a Chloride Solution

Experiment 98-k, pH of the starting solution 1.13; in the solution—40 g/liter of NaCl; hypochlorite: Active Cl, 122 g/liter NaOH 19 g/liter.

Experiment 99-k, pH of the starting solution, 1.16; in the solution—40 g/liter of NaCl, hypochlorite: Active Cl, 122 g/liter, NaOH 19 g/liter.

Temperature	Composition of the solution (g/liter)			E (in V)		Logarithm of the activities		log L_s	log K'
	Co^{++}	Cl^-	pH	During the addition of the hypochlorite	During the determination of pH	Co^{++}	Co^{+++}		
19.0°	44.8	84.6	2.21	1.308	1.288	-0.430	-9.605	-44.775	+2.970
	37.7	79.0	2.14	—	1.338	-0.517	-9.832	-44.432	+2.417
	28.3	75.3	2.25	1.358	1.318	-0.655	-8.650	-43.900	+2.900
	22.0	75.3	2.35	1.368	1.318	-0.762	-9.472	-44.442	+2.422
	11.2	63.4	2.50	1.358	1.288	-1.036	-10.216	-44.716	+2.716
	5.2	53.0	2.78	1.353	1.264	-1.328	-10.918	-44.218	+2.578
	2.58	—	2.83	1.328	1.252	-1.553	-11.348	-44.848	+2.858
	0.70	—	3.20	1.312	1.248	-1.958	-11.828	-44.228	+2.228
81.0	Average							-44.49	+2.709
	39.8	67.5	1.48	1.308	1.226	-0.484	-10.469	-43.869	+6.024
	33.1	63.6	1.52	1.328	1.238	-0.578	-10.428	-43.668	+5.902
	24.4	60.0	1.53	1.308	1.248	-0.718	-10.433	-43.643	+5.843
	20.9	56.0	1.58	1.328	1.238	-0.785	-10.635	-43.695	+5.285
	15.8	54.8	1.61	1.321	1.228	-0.900	-10.900	-43.870	+6.070
	10.62	—	1.83	1.326	1.241	-1.056	-10.836	-43.176	+5.376
	8.50	46.2	1.86	1.318	1.224	-1.143	-11.191	-43.411	+5.611
	7.64	51.9	1.80	1.308	1.247	-1.180	-10.915	-43.315	+5.415
	5.83	54.5	1.73	1.310	1.256	-1.300	-10.870	-43.385	+5.680
	4.56	40.2	1.91	—	1.242	-1.377	-11.177	-43.247	+5.447
	2.74	—	1.95	—	1.248	-1.538	-11.253	-43.203	+5.403
	Average							-43.50	+5.65

The accuracy of the potential measurement was ± 0.002 V. In order to measure the pH of the solution (by means of a potentiometer with glass electrodes), a sample was removed from the pulp after the addition of the determined quantity of hypochlorite. The accuracy of the pH measurement was not lower than ± 0.05 . After the determination of the pH, the sample was filtered, and the concentration of the cobalt and chloride ions determined.

The cobalt solutions were prepared from cobalt sulfate and chloride of Pure for Analysis grade; the solutions were initially purified from iron hydroxide, with cobaltous hydroxide and filtered; the filtrate was acidified with C.P. sulfuric or hydrochloric acid, respectively, to a pH of about 1.2. The sodium hypochlorite solutions were prepared by passing purified chlorine gas into a solution of C.P. sodium hydroxide at temperatures not greater than 15° .

The actual potential was measured at once after the addition of the hypochlorite and the measurements were then continued periodically until stopped changing. A sample of the pulp was then removed, and the pH of the solution measured.

TABLE 2

Changes in Parameters During Precipitation of Cobaltic Hydroxide from Sulfate-Chloride Solutions.
Experiments 95-k, 96-k, 97-k; starting solution of cobalt sulfate without the addition of NaCl; the removal of the sample was conducted at 19.2° after 4 hours, 50.5°, after 1-2 hours, and at 81°, 1.5 hours.

Temperature	Composition of the solution g/liter			E (in V)		Logarithm of the activity		log L ₂	log K'
	Co ⁺⁺	Cl ⁻	pH	During the addition of the hypochlorite	During the determination of pH	Co ⁺⁺	Co ⁺⁺⁺		
19.2°	18.1	9.47	2.40	1.398	1.358	-0.844	-8.821	-43.621	+ 1.621
	11.8	13.85	2.43	1.393	1.358	-1.018	-8.993	-43.693	+ 1.693
	7.25	17.70	2.63	-	1.339	-1.208	-9.508	-43.608	+ 1.608
	5.83	18.50	2.68	-	1.333	-1.276	-9.676	-43.636	+ 1.636
	Average							-43.64	+ 1.642
50.5	20.5	7.53	1.69	1.408	1.328	-0.793	-9.268	-44.098	+ 4.198
	14.5	9.47	1.95	1.398	1.298	-0.932	-9.877	-43.927	+ 4.027
	7.86	12.6	1.76	1.398	1.338	-1.174	-9.489	-44.109	+ 4.209
	3.47	13.8	1.93	1.388	1.337	-1.468	-9.803	-43.883	+ 4.020
	Average							-44.01	+ 4.113
81.0	25.2	6.10	1.40	1.361	1.211	-0.706	-10.966	-44.596	+ 6.756
	20.5	11.25	1.46	1.361	1.262	-0.790	-10.340	-43.750	+ 5.915
	17.3	18.40	1.38	1.351	1.278	-0.864	-10.180	-43.840	+ 8.024
	8.3	20.30	1.45	1.351	1.254	-1.149	-10.809	-44.259	+ 6.414
	2.74	-	1.70	1.361	1.224	-1.553	-11.643	-44.346	+ 6.003
	0.72	-	2.01	1.351	1.228	-1.958	-12.008	-43.778	+ 5.833
	0.095	-	3.30	1.351	1.232	-2.796	-12.766	(-40.646)*	(+ 2.846)*
	Average							-44.15	+ 6.232

TABLE 3

Change in the Parameters During Precipitation of Cobaltic Hydroxide from Sulfate Solutions.
Experiment 92-k; starting solution of CoSO₄ with 40 g/liter of Co; pH 1.06; temperature 80°; hypochlorite: active Cl, 98 g/liter; NaOH, 30 g/liter.

Composition of the solution (g/liter)			E (in V)		Logarithm of the activity		log L ₂	log K'
Co ⁺⁺	Cl ⁻	pH	During the addition of the hypochlorite	During the determination of pH	Co ⁺⁺	Co ⁺⁺⁺		
35.2	(1.3)	1.13	1.437	1.413	-0.547	-7.897	-42.307	+ 4.507
33.6	(2.0)	1.25	1.413	1.402	-0.556	-8.066	-42.116	+ 4.316
32.6	(3.5)	1.28	1.412	1.400	-0.585	-8.135	-42.095	+ 4.295
29.4	5.0	1.32	1.406	1.391	-0.635	-8.310	-41.150	+ 4.350
27.6	6.50	1.36	1.396	1.385	-0.663	-8.418	-42.133	+ 4.333
24.8	(8.0)	1.38	1.392	1.370	-0.704	-8.674	-42.334	+ 4.734
22.0	9.42	1.40	1.385	1.366	-0.762	-8.797	-42.397	+ 4.597
19.9	(10.5)	1.52	1.376	1.355	-0.804	-8.984	-42.224	+ 4.424
18.9	11.57	1.48	1.378	1.357	-0.827	-9.037	-42.397	+ 4.597

* The reason for the extreme deviation from the average values obtained with large concentrations of Co⁺⁺ in the solution is the start of the peroxidation of cobaltic precipitate at pH > 2.5 at the above temperatures [14].

TABLE 3 - (continued)

Composition of the solution (g/liter)			E (in V)		Logarithm of the activity			
Co ⁺⁺	Cl ⁻	pH	During the addition of the hypochlorite	During the determination of pH	Co ⁺⁺	Co ⁺⁺⁺	log L ₂	log K'
16.3	(12.6)	1.50	1.373	1.354	-0.886	-9.041	-42.341	+ 4.541
14.7	13.77	1.47	1.363	1.346	-0.924	-9.239	-42.629	+ 4.829
11.1	(14.7)	1.55	1.361	1.332	-1.036	-9.551	-42.701	+ 4.901
9.65	(15.74)	1.60	1.361	1.335	-1.092	-9.567	-42.567	+ 4.767
8.40	(16.8)	1.60	1.361	1.339	-1.149	-9.564	-42.564	+ 4.764
7.35	17.97	1.52	1.361	1.333	-1.194	-9.694	-42.934	+ 5.134
Average . .							-42.39	+ 4.61

Notes: 1) Samples were taken after 5-10 minutes; 2) figures in parentheses are interpolated values (the same in Tables 4 and 5).

TABLE 4

Change in Parameters During Precipitation of Cobaltic Hydroxide from Chloride Solutions.

Experiment 90-k: starting solution of CoCl₂ with 50 g/liter of Co⁺⁺; temperature 81°; hypochlorite, Cl₂ active 74 g/liter; NaOH 24 g/liter. Experiment 93-k: starting solution of CoCl₂ and NiCl₂ containing 30 g/liter of Co and 60 g/liter of Ni, pH 1.42; temperature 80°; hypochlorite: Cl₂ active 101.4 g/liter; NaOH, 41.6 g/liter

Composition of the solution (g/liter)			E (in V)		Logarithm of the activity			
Co ⁺⁺ /Cl ⁻	Cl ⁺⁺⁺	pH	During the addition of the hypochlorite	During the determination of pH	Co ⁺⁺	Co ⁺⁺⁺	log L ₂	log K'
40.3	72.4	1.83	1.306	1.273	-0.491	- 9.88	-42.190	+ 4.390
34.5	63.4	1.73	1.316	1.298	-0.650	- 9.79	-42.300	+ 4.500
27.7	63.4	1.80	1.306	1.303	-0.664	- 9.614	-42.014	+ 4.214
22.5	-	1.82	1.320	1.306	-0.754	- 9.664	-42.004	+ 4.204
18.3	63.4	1.88	1.320	1.303	-0.838	- 9.80	-41.960	+ 4.160
14.7	-	1.85	1.318	1.302	-0.924	- 9.89	-42.140	+ 4.340
11.2	54.3	1.96	1.322	1.311	-1.036	- 9.89	-41.810	+ 4.010
9.10	-	1.95	1.326	1.305	-1.114	-10.04	-41.990	+ 4.190
5.25	60.4	1.93	1.324	1.311	-1.319	-10.17	-42.180	+ 4.380
3.65	-	1.98	1.326	1.314	-1.456	-10.26	-42.120	+ 4.320
1.04	-	2.07	1.328	1.324	-1.842	-10.50	-42.090	+ 4.290
0.66	-	2.30	1.296	1.269	-1.958	-11.39	-42.290	+ 4.490
Average							-42.00	+ 4.29
25.8	101.4	1.50	1.333	1.316	-0.695	- 9.445	-42.745	+ 4.945
22.4	(104)	1.56	1.320	1.314	-0.757	- 9.527	-42.647	+ 4.847
19.5	107.7	1.57	1.322	1.311	-0.812	- 9.632	-42.722	+ 4.922
15.9	(97)	1.70	1.325	1.321	-0.896	- 9.561	-42.261	+ 4.461
14.8	86.9	1.58	1.333	1.326	-0.921	- 9.531	-42.591	+ 4.791
13.6	(85.4)	1.70	1.331	1.317	-0.955	- 9.685	-42.385	+ 4.585
12.1	84.0	1.78	1.328	1.315	-1.000	- 9.755	-42.215	+ 4.415
10.9	83.2	1.77	1.326	1.311	-1.046	- 9.866	-42.356	+ 4.556
10.1	82.5	1.85	1.334	1.310	-1.076	- 9.898	-42.148	+ 4.348
Average							-42.45	+ 4.65

Notes. In both experiments, the samples were removed after ten minutes.

A state close to equilibrium was usually established at room temperature after 1.5-2 hours, and at higher temperatures (50-80°), after 30-60 minutes.

In order to judge the state of the process under conditions approximating the industrial, in a series of

experiments, the removal of the samples and the basic measurements (E and pH) were conducted 5-10 minutes after the addition of each portion of the hypochlorite. The results of the experiments are given in Tables 1-5.

The activity coefficients of CoSO_4 and CoCl_2 were taken from data [15, 18]. The calculation of L_2 and K_1^* for temperatures above room temperature, required a knowledge of the value of the normal potential of $\text{Co}^{++} \rightarrow \text{Co}^{+++}$ and the ion product of water. $E_{\text{Co}^{++}/\text{Co}^{+++}}$ at 20° was taken as being equal to 1.82 V, and the temperature coefficient, 0.00168 V per degree [4, 17]; $E_{\text{Co}^{++}/\text{Co}^{+++}}$ for 50° was obtained as 1.87 V and 1.93 V for $80 \pm 1^\circ$ by extrapolation. The value of the ion product of water for various temperatures was taken from [19].

The activity of the Co^{+++} was calculated with equation (12), the logarithmic hydrolysis constant of Co^{+++} by equation (20), and the activity product $L_2 \text{Co}(\text{OH})_2$ from equation (13).

All the values calculated on the basis of experimental data are given in the same Tables (1-5).

TABLE 5

Change in the Parameters During Precipitation of Cobaltic Hydroxide from Sulfate Solutions

Experiment 94-k; starting solution CoSO_4 ; pH 1.06; Hypochlorite $\text{Cl}^{\text{active}}$ 90.4 g/liter; NaOH 32 g/liter; temperature, 80° . The samples were removed after 5-10 minutes.

Composition of the solution (g./liter)			E (in V)		Logarithm of the activity				
Co ⁺⁺	Cl ⁻	pH	During the addition of the hypo-chlorite	During the determina-tion of pH	Co ⁺⁺	Co ⁺⁺⁺	log L ₂	log K [*]	
33.8	(2.1)	1.15	}	1.344	-0.568	- 8.898	-42.248	+ 5.448	
31.5	4.35	1.26		1.350	-0.600	- 8.850	-42.870	+ 5.070	
29.1	-	1.28		1.334	-0.638	- 9.018	-43.158	+ 5.178	
24.4	24.3	1.40		1.335	-0.719	- 9.199	-42.799	+ 4.999	
22.0	(25)	1.40		1.326	-0.762	- 9.312	-42.912	+ 5.112	
20.5	25.4	1.43		1.318	-0.790	- 9.500	-43.010	+ 5.210	
18.6	(26)	1.45		1.319	-0.832	- 9.532	-42.982	+ 5.182	
14.5	30.0	1.46		1.299	-0.932	- 9.932	-43.352	+ 5.552	
12.1	34.0	1.52		1.284	-1.005	-10.205	-43.445	+ 5.645	
11.3	(36)	1.53		1.300	-1.032	-10.002	-43.212	+ 5.412	
8.8	37.6	1.63		1.294	-1.125	-10.185	-43.095	+ 5.235	
7.90	(42.0)	1.66		1.301	-1.168	-10.118	-42.938	+ 5.138	
3.87	(53)	1.71		1.305	-1.432	-10.332	-43.002	+ 5.202	
2.86	53.6	1.78		1.288	-1.538	-10.688	-43.148	+ 5.348	
2.12	(54)	1.82		1.288	-1.620	-10.800	-43.140	+ 5.340	
1.01	55.8	2.00		1.294	-1.854	-10.904	-43.704	+ 4.904	
							Average	- 42.98	+ 5.31

Because in these experiments sodium hypochlorite was used as the oxidizing agent, and a certain amount of gaseous chlorine is evolved from the solution in the process of oxidizing cobalt, then the following processes participate in the generation of the compromise (actual) potential in the solution:



The corresponding equations for the actual redox potential of each of these reactions are as follows:

$$E = E_0^{\text{Cl}_2/\text{Cl}_2^-} - \frac{RT}{nF} \ln \frac{a_{\text{Cl}^-}}{a_{\text{Cl}_2}} \quad (22')$$

$$E = E_0^{\text{Cl}^-/\text{HClO}} - \frac{RT}{nF} \ln \frac{a_{\text{Cl}^-}}{a_{\text{HClO}} a_{\text{H}^+}} \quad (23')$$

• No measurements made.

$$E = E_0^{\text{Cl}_2/\text{HClO}} - \frac{RT}{nF} \ln \frac{a_{\text{Cl}_2}}{a_{\text{HClO}} \cdot a_{\text{H}^+}} \quad (24')$$

In order to make possible an examination of the effect of the various factors determining the E and pH during the precipitation of the cobalt [16], the measurement of E and pH was conducted in dilute solutions of sulfuric acid during titration with hypochlorite solution. The results of the experiments are shown on Figs. 1 and 2.

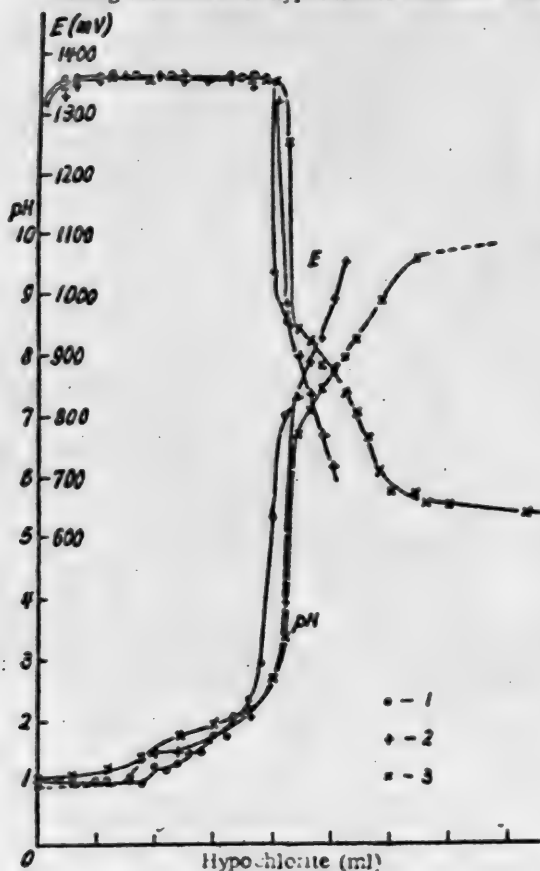


Fig. 1 Effect of the temperature on the change in E and pH during titration of 1/5 $\text{N}_2\text{H}_4\text{SO}_4$ (with the addition of 40 g/liter of NaCl) with an alkaline solution of sodium hypochlorite.

1) At 24°; 2) at 50°; 3) at 80°.

tion of the hypochlorite are also very similar. All of this indicates that the system of solution-precipitate for cobaltic hydroxide approaches a state close to the equilibrium within a very short time.

It is also apparent from these results that the activity coefficient $L_a \text{Co(OH)}_2$ increases with the temperature (Table 1); a considerable sorption of the sulfate ion by the precipitate occurs in the sulfate solutions which somewhat distorts the picture of the change of L_a during the increase in temperature (Table 2); Thus the weight ratio of $\text{Co}^{+++} : \text{SO}_4^{--}$ in precipitates obtained at about 80°, varied from 1:0.1 to 1:0.2, while at lower temperatures, the sorption of the SO_4^{--} was still higher.

For this reason, the most reliable of all of the thermodynamic values were given by experiments in chloride solutions because the side processes (sorption of the anion) were at a minimum.

Considering the above, the following values (according to Table 1) can be accepted for the activity product of Co(OH)_2 for temperatures: 19° $L_a^{19} = 3.2 \cdot 10^{-45}$, 81° $L_a^{81} = 3.2 \cdot 10^{-44}$.

Increase of the equilibrium constant (K') of the hydrolysis reaction of Co^{+++} with the increase of the

- The actual potential was always recalculated versus the hydrogen electrode.

As it was expected from equations (22'), (23'), (24'), the actual redox potential of the solution at pH below 3 (i.e., in the pH region of the precipitation of cobaltic hydroxide at 19-81°), decreased with the increase of the concentration of Cl^- in solution, and as the experiment showed, did not vary with the pH and the temperature of the solution.

Returning to Tables 1-5, it is apparent that E_0 and its tendency to change with the time of the oxidation-precipitation of cobalt with hypochlorite indicates that hypochlorous acid, not containing cobalt, is found in the solution: the greater the concentration of the chloride ion in the cobalt solutions, the lower is E at the time of the precipitation of the cobalt, the weaker, therefore, the oxidizing ability of the hypochlorite in such solutions.

Fig. 3 shows that, in accordance with equation (16), the decrease of the oxidizing strength of the agent used leads to a shift of the curves of the equilibrium values of the pH during the precipitation of cobalt in the region of higher pH values, while Figs. 3, 4, and 5 confirm the completely obvious relation between the pH and the concentration of the bivalent cobalt during the oxidation of the latter to the trivalent, and the formation, in equilibrium with a solution, of the precipitate of Co(OH)_2 . It is apparent on these same figures, that, with increase in temperature of the pulp, the curve of the equilibrium value of pH is sharply shifted into the region of more acidic solutions.

It is apparent from Tables 1-5 that the values of $\log K'$ and $\log L_a$ show a small variation from the average during the extending of the precipitation time, and that the corresponding values for removal of samples after 5-10 minutes and after 1-1.5 hours after the addition

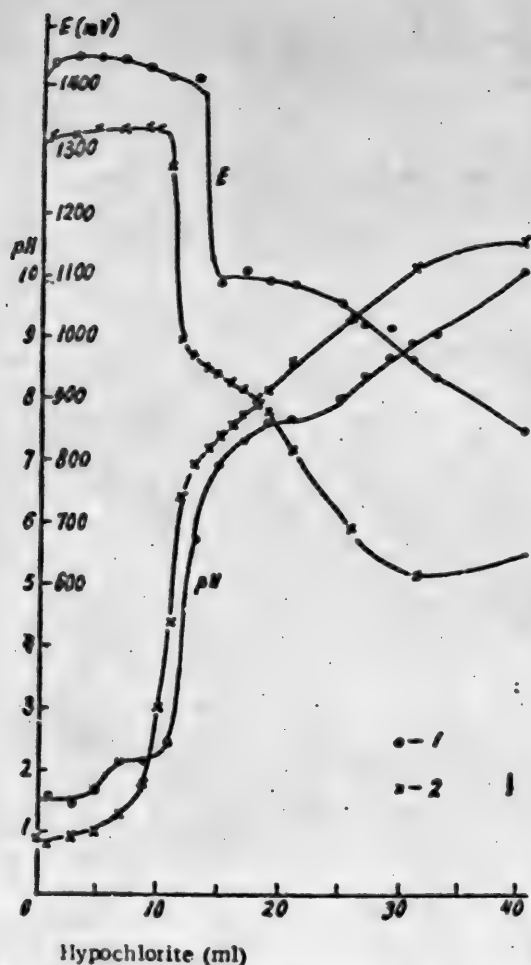


Fig. 2. Effect of the concentration of the chloride ion on the change of E and pH during titration of a 1/10 N H_2SO_4 with an alkaline solution of sodium hypochlorite. 1) Without NaCl in the starting solution; 2) with 200g/liter of NaCl.

temperature indicates the endothermic character of the reaction.

The following value is obtained for the reaction in chloride solutions using the data in Table 1.

$$Q_1 = -22500 \text{ cal.}$$

while from the data of other pairs of experiments (100-k and 101-k), the results of which are not given in consideration of economy of space, the following values were obtained for the value of Q_1 : for the temperature interval 19.0-50.2°, 33,900 cal; 50.2-81.0°, 36,200 cal; 19.0-81.0°, 35,000 cal. Therefore, the heat effect of the formation of $Co(OH)_3$ from the elements has the following value (in the interval 19-81°): for precipitation from chloride solutions, +236,980 cal/mole, for precipitation from sulfate solutions, +249,180 cal/mole.

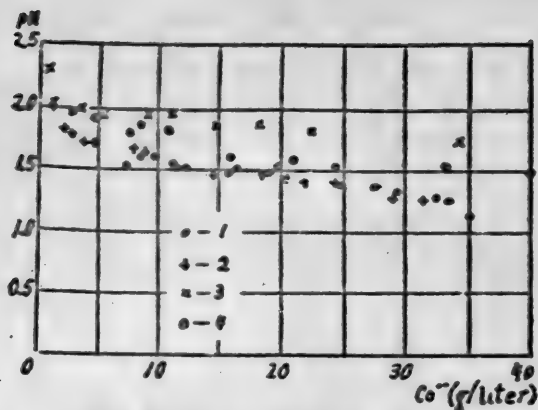


Fig. 3. The effect of the presence of the chloride ion in cobalt solutions on the change of the position of the equilibrium pH curve of the solution during the precipitation of cobaltic hydroxide with sodium hypochlorite. 1-2 Sulfate solutions; 3-4 chloride solutions.



Fig. 4. Effect of temperature and concentration of Co on the equilibrium pH value of the solution during the precipitation of cobaltic hydroxide.

1) Experiment No. 95, at 19°; 2) experiment No. 96, at 50°; 3) experiment No. 97, at 81°.

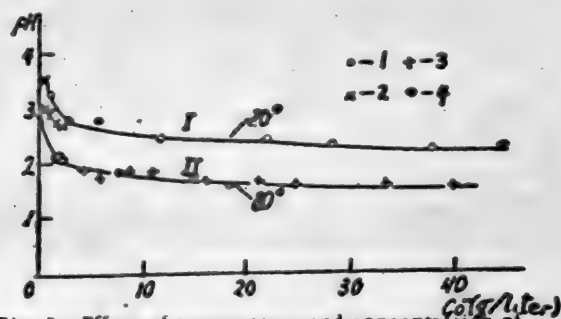


Fig. 5. Effect of temperature and concentration of Co on the equilibrium pH value of the solution during the precipitation of cobaltic hydroxide with sodium hypochlorite.

1) Experiment No. 98-k; 2) experiment No. 100-k; 3) experiment No. 90-k; 4) experiment No. 101-k. I - at 20°; II - at 80°.

The greater value of the value Q obtained for the precipitation cobaltic hydroxide from sulfate solutions can be explained by the slight shift of the equilibrium between the solution and cobaltic hydroxide as a result of the exothermic process and the sorption of the sulfate ion by the precipitate. The calculations did not take into account the other exothermic process, the hydration of the precipitate; usually, this is small according to the absolute value of the effect.

The very large absolute value of Q is supplementary proof that cobalt hydroxide precipitate is a gel, and not a crystalline solid [14] because of which a considerable store of internal energy remains unliberated.

Laboratician N. N. Ilyin participated in the investigation.

SUMMARY

1. An electrochemical method for the investigation of phenomena occurring during the process of the precipitation of cobaltic hydroxide was used, the relationships of the variation of the equilibrium pH values of the solution with temperature and concentration of the bivalent cobalt in chloride and sulfate solutions was studied, and the effect of the value of the redox potential of the oxidizing agent was shown.

2. The results obtained favor the representation of the formation of cobaltic hydroxide by the action of strong oxidizing agents as the oxidation of Co^{2+} to Co^{3+} , and the subsequent hydrolysis of the salts of the trivalent cobalt.

3. More accurate values of the activity product and the heat of formation of cobaltic hydroxide were obtained.

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Received December 8, 1952

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PHYSICO-CHEMICAL ANALYSIS OF SYSTEMS WITH INDIUM SULFATE

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The development of experiments on the study of the processes of complex formation in solution for the determination of composition and molecular state of the complex compounds stimulated great interest in the investigation of systems of the type A-B-solvent with various methods of physico-chemical analysis, which resulted in the development of new methods for the investigation of such systems [1].

In the present communication basic results are reported of the physico-chemical investigation of systems of indium sulfate-sulfuric acid (or ammonium sulfate) in aqueous solutions.

Indium sulfate is comparatively readily soluble in water. From neutral solutions, this salt crystallizes with nine, and according to more recent results [2], with ten molecules of water, $\text{In}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$. From solutions containing sulfuric acid, a product of the addition of $\text{In}_2(\text{SO}_4)_3$ with sulfuric acid precipitates, which is regarded in the literature as the complex acid $\text{HIn}(\text{SO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ analogous to the crystallo-hydrate of the same type of compound of thallium $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [3], or as the acid salt $\text{InH}(\text{SO}_4)_2$ [4]. Indium sulfate forms double salts with a series of monovalent metals (and ammonium) of the general type $\text{MeIn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{MeIn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [5]. The number of molecules of water of crystallization to a great degree depends on the nature of the monovalent metal and the conditions of crystallization of the salts. For example, the following salts of this type were obtained: $\text{K}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ [5], $\text{Rb}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, $\text{Cs}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ [6], $(\text{NH}_4)_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ [7].

All of these salts are formed by the mixing of concentrated solutions of these components taken in equimolecular ratios. These salts are readily soluble. Hydrolysis occurs upon boiling the solutions [5, 6].

Double salts with alkyl substituted ammonium cations are also known, as for example: $(\text{CH}_3\text{NH}_3)_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, $2(\text{C}_2\text{H}_5\text{NH}_3)_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, $3(p\text{-C}_2\text{H}_5\text{NH}_3)_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ and several others [8]. These salts possess great stability to heat. Their melting points are over 300° . In a series of cases, these salts also possess optical activity. Analogous complex halide salts of substituted ammonium bases (in contrast to the sulfates) crystallize without water, for example: $2(\text{C}_2\text{H}_5)_4\text{NCl} \cdot \text{InCl}_3$, $2(\text{CH}_3)_4\text{NBr} \cdot \text{InBr}_3$, and others [8].

All of the above mentioned double salts of indium sulfate were studied mainly for preparative purposes, to develop a method for the preparation of these salts out of solution certain physico-chemical properties such as: melting point, solubility, etc., were also investigated.

Solutions of these salts had scarcely been investigated in the physico-chemical sense. This remark is also true for systems of indium sulfate-sulfuric acid-water.

Ensslin [2], studying the system $\text{InC}_3\text{SO}_3\text{-H}_2\text{O}$ by method of solubility and densities, established that the following sulfates are formed in this system at temperatures between 20 and 60° : $\text{In}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ($n = 10, 6, 5, 4$); $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; $2\text{In}(\text{OH}) \cdot (\text{SO}_4) \cdot 5\text{H}_2\text{O}$.

The decahydrate, $\text{In}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ is a white readily soluble salt. According to Ensslin, it is formed in solutions containing from 10 to 20 weight % of free sulfuric acid. Solutions containing less than 3% of the acid result in the formation of basic salts. At a concentration of sulfuric acid greater than 30%, a salt of the composition $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ is formed, which precipitates in the form of shiny white tablets or plates. Crystallization occurs at room temperature.

The anhydrous salt of indium sulfate is obtained by heating $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ to 250° .

EXPERIMENTAL

The problems of the present investigation were to study the possibility of using electroconductivity (and cryoscopy) as a method of physico-chemical analysis of systems of the type A-B solvents, to establish whether or

TABLE 1

The Specific Electroconductivity of the System $\text{In}_2(\text{SO}_4)_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$:
0.1 molar solution

Mole % $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$	Specific electroconductivity $\times 10^3$ (found) at t°				Specific electroconductivity $\times 10^3$ (calculated) at t°			
	0	20	30	40	0	20	30	40
0	31.28	42.30	45.61	49.46	31.28	42.30	45.61	49.46
20	25.23	34.40	37.42	40.30	26.68	35.30	39.37	42.76
40	20.32	27.55	29.78	32.19	22.08	30.37	38.14	36.22
50	18.02	24.42	26.57	28.53	19.78	27.39	30.03	33.85
60	15.83	21.44	23.68	25.46	17.49	24.40	26.91	29.60
100	8.29	12.48	14.46	16.36	8.29	12.48	14.46	16.36

TABLE 2

Specific Electroconductivity of the System $\text{In}_2(\text{SO}_4)_3 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$:
0.1 M molar solution

Mole % $\text{In}_2(\text{SO}_4)_3 / (\text{NH}_4)_2\text{SO}_4$	Specific electroconductivity $\times 10^3$ at t°					
	Measured			Calculated		
	20	30	40	20	30	40
0	16.60	19.87	23.30	16.60	19.87	23.30
10	15.70	18.81	22.02	16.17	19.33	22.61
20	15.15	—	21.00	15.78	—	21.91
30	14.45	17.06	19.73	15.36	18.25	21.01
40	13.96	16.35	18.80	14.95	17.71	20.52
50	13.46	15.74	18.04	14.54	17.16	19.83
60	13.26	15.45	17.62	14.13	16.62	19.14
70	12.94	15.15	17.16	13.72	16.08	18.44
80	12.73	14.84	16.84	13.22	15.54	17.74
100	12.48	14.46	16.36	12.48	14.46	16.36

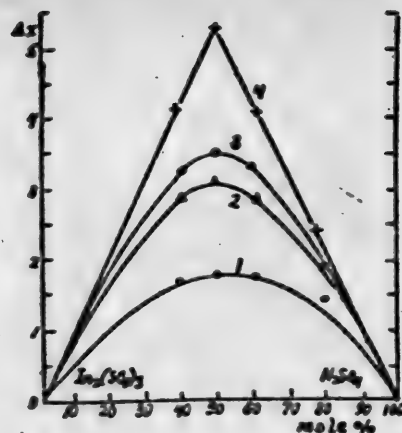


Fig. 1. Deviation of the specific electroconductivity of the system $\text{In}_2(\text{SO}_4)_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$

1) 0° ; 2) 20° ; 3) 30° and 4) 40° and a total concentration of 0.1 molar.

not complex compounds are formed in this type of system, to determine the composition of these complex compounds directly in solution, and to study the effect of temperature and concentration of the solution upon the isothermal electroconductivity curves. The experi-

mental results of the investigation of the systems $\text{In}_2(\text{SO}_4)_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ and $\text{In}_2(\text{SO}_4)_3 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ by the method of electroconductivity and cryoscopy are given below.

Anhydrous indium sulfate, $\text{In}_2(\text{SO}_4)_3$, was obtained by the heating of its salt $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ which was obtained by the solution of chemically pure In_2O_3 in an excess of sulfuric acid, according to Ensslin's data [2]. The solution obtained was evaporated on the water bath until the formation of the salt which was filtered on a porcelain funnel.

Then the salt $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ in the porcelain dish was dehydrated in a muffle furnace by raising the temperature gradually to $230-250^\circ$ until the complete removal of SO_3 vapors, and then was kept at this temperature for some time. With such a method for the dehydration of the salt and the removal of sulfuric acid (complexly bound), a cloud of vapors of SO_3 is created over the dish of the indium sulfate in the muffle furnace, which prevents the formation of basic salts during the dehydration.

The anhydrous salt, $\text{In}_2(\text{SO}_4)_3$, obtained in this manner, had the form of a white powder. Analytical results: In - 44.00%, SO_4 - 56.05%; calculated for $\text{In}_2(\text{SO}_4)_3$: In - 44.33%, SO_4 - 55.67%.

The rest of the preparations were C. P., or correspondingly purified.

The measurement of the electroconductivity, and the graphic representation of the results were effected according to Ostromyslensky's and Dzhob's method.

The application of electroconductivity as a method of physico-chemical analysis according to Ostromyslensky-Dzhob was first used by I. A. Sheka and A. I. Goldinov for the investigation of the system $(\text{NH}_4)_2\text{SO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ [9]; then this method was used and developed in other investigations of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukr. SSR. The usual technique for the measurement of the electroconductivity was used (with a vacuum tube signal generator). The temperature was kept within the limits of variation of $\pm 0.05^\circ$ by means of a thermostat.

* The calculation of the additive electroconductivity was made according to the rule of combination.

1. Table 1 gives the results of the measurement of the specific conductivity of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at temperatures of 0, 20, 30 and 40° and a total concentration of 0.1 molar. Fig. 1 gives the deviation of the specific electroconductivity from additivity.

Fig. 2 gives the specific electroconductivity and deviation from additivity of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at 40° and a total concentration of 0.05 molar.

The magnitude of the deviation of the specific electroconductivity from additivity ($\Delta\kappa$) was found by the subtraction of the found values of the specific electroconductivity from the calculated.

From the results in Table 1 and Figs. 1 and 2, it is found that the specific electroconductivity of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ increases with the increase of the total concentration (0.05-0.1 molar) of the system. The deviation from additivity, the maximum of which corresponds to equimolecular ratio of $\text{In}_2(\text{SO}_4)_3$ and H_2SO_4 for a 0.1 molar solution, has a greater value than for 0.05 molar solutions. At temperatures from 0-40°, the deviation from additivity increases with the temperature and the total concentration of the solution. On the basis of the above electroconductivity measurements, it can be concluded that a compound of the composition: $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ exists in the solution at the temperatures and concentrations investigated. A cryoscopic investigation of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was conducted by a method reported in a paper by Ya. A. Fialkov and I. D. Muzyka [10].

To 5 ml of an 0.1 molar solution of sulfuric acid were added increasingly greater, by weight, samples of $\text{In}_2(\text{SO}_4)_3$, and each time the depression was measured; the depression of the initial solution of sulfuric acid was arbitrarily taken as zero.

The results of the measurements are given on Fig. 3.

As is apparent from Fig. 3, there is an inflection on the change of depression curve in the region of an equimolecular ratio of $\text{In}_2(\text{SO}_4)_3$ and H_2SO_4 . Later the path of the curve is determined by a linear relationship with the concentration of indium sulfate. The results of the cryoscopic measurement confirmed, therefore, the previously drawn conclusion, on the basis of the measurement of the electroconductivity, of the formation of the compound $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ in the solution.

2. The system $\text{In}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$. A physico-chemical analysis of this system was made by the method of electroconductivity in the temperature interval of 20-40°.

The results of the investigation are given in Table 2 and Fig. 4.

The results in Table 2 and Fig. 4 indicate that a compound of the equimolar composition $\text{In}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ exists in the system indium sulfate-ammonium sulfate-water: (as in the solid phase); where, as in the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the value of the deviation from additivity increases with the temperature.

For the solution of the problem of the structure of the complex compound $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ and the nature of the ions in the solution, experiments were set up on the transport of ions in solutions of $\text{In}_2(\text{SO}_4)_3$ (1), as well as $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ (2).

0.5 molar solutions were investigated. The electrolyzer consisted of three sections: the cathodic, the anodic, and the intermediate. Platinum electrodes were used. The feed bath was a direct current from the panel of a storage

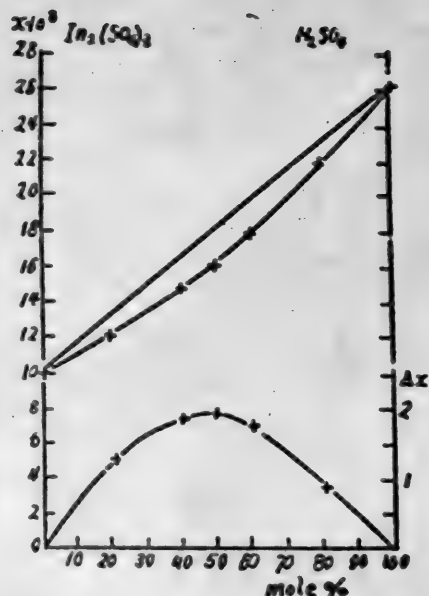


Fig. 2. Specific conductivity and deviation from additivity of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at 40° and a total concentration of 0.05 molar.

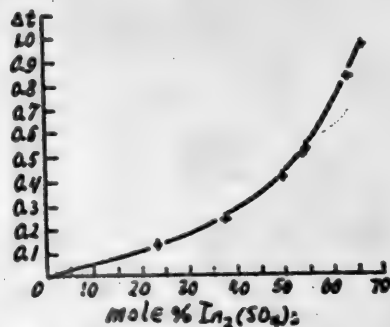


Fig. 3. Cryoscopy of the system $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

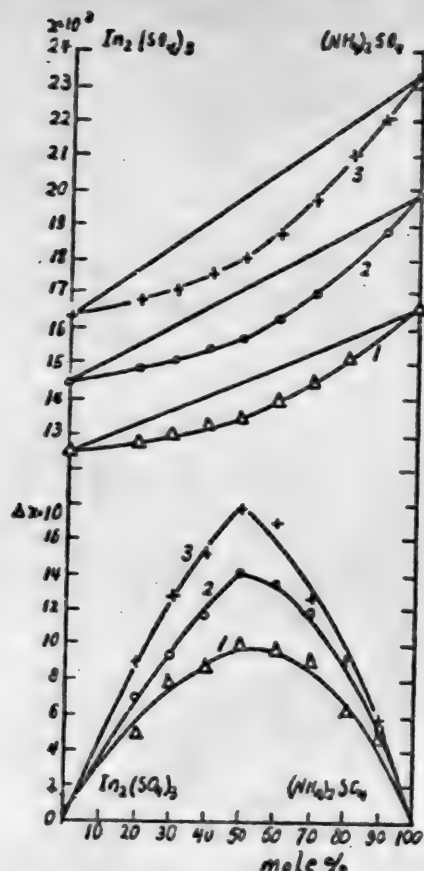


Fig. 4. Specific electroconductivity and deviation from additivity of system $\text{In}_2(\text{SO}_4)_3-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$. 1) 20° ; 2) 30° , and 3) 40° and total concentration of 0.1 molarity.

within a wide temperature interval, the optimum temperature conditions for the formation and existence of complex compounds in solution could be established.

4. On the basis of the investigation conducted, it is possible to conclude that a compound $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ existed in solution in the system indium sulfate-sulfuric acid-water, and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3$ in the system indium sulfate, ammonium sulfate-water, solvated, apparently, by a determined amount of water molecules.

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battery. Current strength 15-30 mA. Duration of the experiments, 3-24 hours. The quantitative determination of indium was effected gravimetrically (as In_2O_3).

It was established that the transport number of indium to the cathode, upon going from electrolyte 1 to electrolyte 2, decreases by more than 2 times, from 0.16 to 0.06. In order to explain these facts it can be supposed that solutions of indium sulfate have a complex structure; complex ions are present in these solutions in which, evidently, indium also enters into the composition of the anions.

The introduction of sulfuric acid into the system $\text{In}_2(\text{SO}_4)_3-\text{H}_2\text{O}$ favors the stabilization of these complex anions, and shifts the equilibrium in the direction of their formation, because of which, the transport number of indium to the cathode decreases sharply almost to zero.

Therefore, there is a basis for proposing that the complex anion of the composition $\text{In}(\text{SO}_4)_2$ is formed in the system $\text{In}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$.

In conclusion, the author wishes to express profound gratitude to Prof. Ya. A. Fialkov for many valuable suggestions during this investigation.

SUMMARY

1. A physico-chemical analysis of the system $\text{In}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ was effected by the method of electroconductivity and cryscopy, and the system $\text{In}_2(\text{SO}_4)_3-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$, by the method of electroconductivity.

2. It was shown that a maximum value for deviation from additivity is found on the electroconductivity isotherm, which corresponds to an equimolar ratio of the components.

The deviation of the electroconductivity from the additive value in these systems increases with the temperature, (in the temperature interval studied) as well as with the concentration of the starting solutions.

3. By conducting, in this manner, an investigation

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Received December 26, 1952

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CRYOSCOPY OF THE SYSTEM ALUMINUM CHLORIDE-ACETAMIDE-NITROBENZENE

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Aluminum halides possess the property to form a complex compounds with almost all classes of organic and inorganic compounds. Complex compounds of aluminum halides and acetamide are not reported in the literature. Meanwhile it seemed of interest to study the role of acetamide as an addend in complex formation reactions.

The character of bond of acetamide with the complex former remains unknown. A. Werner [1] considers that the bond is possible because of oxygen in the carbonyl group. B. N. Menshutkin [2], investigating acetamide complexes of magnesium bromide and iodide [3], considered that the relative stability of acetamide complexes was favored by the presence of the amido group. I. I. Chernyshev and L. A. Nazarov [5] showed that acetamide formed compounds of the inner complex type with salts of bivalent platinum salts with a valence bond resulting from the hydrogen of the amide group.

Physico-chemical investigations of systems containing acetamide and nitrobenzene were conducted by M. S. Ashkinazi [6], as well as by Ya. A. Fialkov and I. D. Muzyka [7] who showed that acetamide in nitrobenzene forms a compound $\text{CH}_3\text{CONH}_2 \cdot \text{Br}_2$ with bromine [6], and $\text{CH}_3\text{CONH}_2 \cdot \text{ICl}$ with iodine chloride [7].

The ternary system aluminum chloride-acetamide-nitrobenzene was studied by the method of cryoscopy. As V. V. Udovenko [8] and Ya. A. Fialkov and I. D. Muzyka [9] showed, cryoscopy is an effective method for the physico-chemical analysis of liquid systems.

EXPERIMENTAL

Commercial anhydrous aluminum chloride was sublimed and was stored in sealed test tubes. Nitrobenzene was allowed to stand for several days with a small amount of bromine, washed with sodium carbonate solution and water, dried over fused calcium chloride, and distilled. The fraction boiling over a one degree range was collected in the receiving tube which was rapidly sealed. The acetamide was recrystallized from alcohol, dried at 50-60°, and was stored in sealed test tubes.

The freezing point was determined in a Beckman apparatus equipped with a magnetic stirrer. Two series of experiments were conducted, with concentrations of aluminum chloride in nitrobenzene of 0.1 to 0.216 moles of AlCl_3 per 1000 g of nitrobenzene. Because of the hygroscopicity of the solutions, the addition of acetamide was done each time with new portions of a nitrobenzene solution of aluminum chloride. Acetamide is not readily soluble in nitrobenzene but in solutions of aluminum chloride, the solubility of acetamide increases in proportion to the concentration of aluminum chloride in the solution. The concentration of acetamide was increased up to a molar ratio of $\text{CH}_3\text{CONH}_2 : \text{AlCl}_3 = 1.2:1$.

The results of the measurements are given in Tables 1 and 2.

TABLE 1

0.1 Moles of AlCl_3 per 1000 g of Nitrobenzene (1.31%)

CH_3CONH_2 AlCl_3 (in moles)	Freezing point according to Beckmann	Δt from that of nitrobenzene	CH_3CONH_2 AlCl_3 (in moles)	Freezing point according to Beckmann	Δt from that of nitrobenzene
Nitrobenzene	3.935°	0°	0.808	3.368°	0.567°
0	3.404	0.531	0.902	3.415	0.520
0.194	3.400	0.535	0.938	3.415	0.520
0.400	3.409	0.526	1.000	3.457	0.478
0.501	3.394	0.541	1.151	3.508	0.427
0.624	3.380	0.555	1.203	3.519	0.416

TABLE 2

0.216 Moles of AlCl_3 per 1000 g of Nitrobenzene (2.8 %)

CH_3CONH_2 AlCl_3 (in moles)	Freezing point according to Reckman	Δt from that of nitrobenzene	Δt calculated
Nitrobenzene	3.023°	0°	0°
0	1.617	1.406	1.406
0.204	1.615	1.408	1.652
0.402	1.555	1.468	1.893
0.500	1.557	1.466	2.011
0.599	1.542	1.481	2.128
0.800	1.539	1.484	2.374
0.899	1.631	1.392	2.493
1.002	1.660	1.363	2.616
1.118	1.772	1.251	2.756

DISCUSSION OF RESULTS

As it is apparent from the Figure, the depression increases very insignificantly at first with the addition of acetamide to the nitrobenzene solution of aluminum chloride, and upon acquiring a concentration of acetamide equal to 0.8 moles per mole of AlCl_3 , the depression decreases.

The insignificant rise in the depression in the region of small concentrations of acetamide, which is more noticeable for more concentrated solutions of aluminum chloride, is apparently due to the hydrolysis of the solution, which could not be avoided in spite of the precautions taken.

The depression was calculated assuming that a reaction did not occur between the aluminum chloride and acetamide. The results of the calculations are given in Table 2 column 4 (Δt_{calc}). From these results, it follows

TABLE 3

The Depression of Solutions of Acetamide in Nitrobenzene

Nitrobenzene (in g)	Acetamide (in g)	Molality of the solution	Δt	Molar depression in freezing point
65.286	0.319	0.023	0.446°	5.4°
39.004	0.124	0.054	0.316	5.8
			Average	5.6

actually it was 0.078°. Therefore, the depression of the solutions up to a concentration of acetamide equal to 0.8, can be considered practically constant. The acetamide added to the solution of aluminum chloride combines chemically, which is also shown by the increase of the solubility of acetamide in nitrobenzene solutions of aluminum chloride.

At molar concentrations of acetamide of 0.8 moles per mole of AlCl_3 , the depression starts to decrease. The path of the curve, of the relation between Δt — composition shows that aluminum chloride forms a complex with acetamide of the composition 1:1. According to B. I. Menshutkin's [11] data, aluminum chloride forms two compounds with nitrobenzene: $\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$ and $\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$. The shift of the maximum on the Δt — composition curve is related with the state of equilibrium between nitrobenzene and acetamide complexes of aluminum chloride, and possibly, with the formation of a ternary complex containing nitrobenzene and acetamide. The decrease in depression is due to the association of the acetamide complex, and apparently, to the simultaneous occurrence of the decrease of the electrolytic dissociation of the complex. The calculated molecular weight of the acetamide complex with nitrobenzene for 0.1-0.2 molal solutions has an average value of 244. According to the formula $\text{AlCl}_3 \cdot \text{CH}_3\text{CONH}_2$ it is 192. The degree of association is 1.27.

These results are shown graphically on the Figure. The concentration of acetamide (in moles) per mole of AlCl_3 is laid off on the abscissas, and the depression in temperature, on the ordinates. The depression of solutions of acetamide in nitrobenzene were also determined. The results of the measurements are given in Table 3.

The molar depression in the freezing point K was calculated by the formula

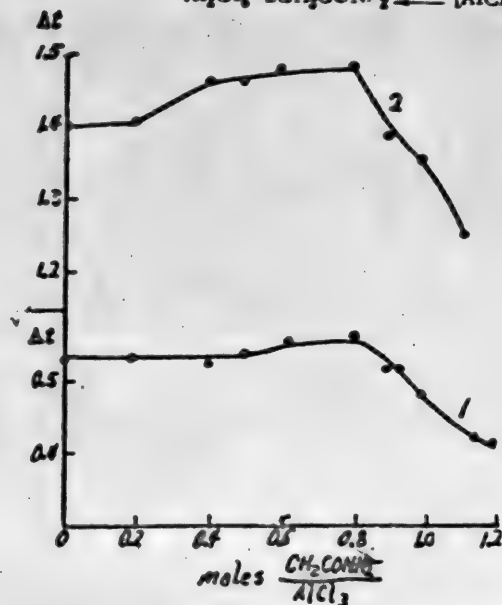
$$K = \frac{\Delta t}{n}, \text{ where } n \text{ is the molarity of the solution.}$$

The cryoscopic constant of nitrobenzene is 6.9° [10]. Therefore, acetamide is somewhat associated in nitrobenzene, and the degree of

$$\text{association } \alpha = \frac{6.9}{5.6} = 1.2.$$

For solutions with a concentration of acetamide of 0.8 moles per mole of AlCl_3 , the calculated increase in the depression is 0.968°.

According to the views of N. N. Lebedev [12], complex compounds of aluminum chloride with organic substances exists in the form of ion pairs which shows a double molecular weight in concentrated solution. In dilute solutions, the dimer dissociates into ions according to the scheme:



The association of the complex must, therefore, be related to the degree of electrolytic dissociation. This can be confirmed by the study of the electroconductivity of the system.

SUMMARY

1. The depression in freezing point of 0.1 and 0.2 molal solutions of aluminum chloride in nitrobenzene-acetamide at a concentration of 0 to 1.2 moles of acetamide per mole of AlCl_3 was investigated. The Δt -concentration of acetamide diagram was constructed from these results.

2. The depression remains practically constant up to a concentration of the acetamide of 0.8 mole per mole of AlCl_3 , during the addition of acetamide to a nitrobenzene solution of aluminum chloride, then the depression decreases.

3. The decrease of the depression is caused by the association of the complex of composition 1:1 formed in the solution. The molecular weight of the acetamide complex is 244. The degree of association is 1.27.

Cryoscopy of the System $\text{AlCl}_3\text{--CH}_3\text{CONH}_2\text{--C}_6\text{H}_5\text{NO}_2$.

1) 0.1 moles of AlCl_3 ; 2) 0.216 moles of AlCl_3 .

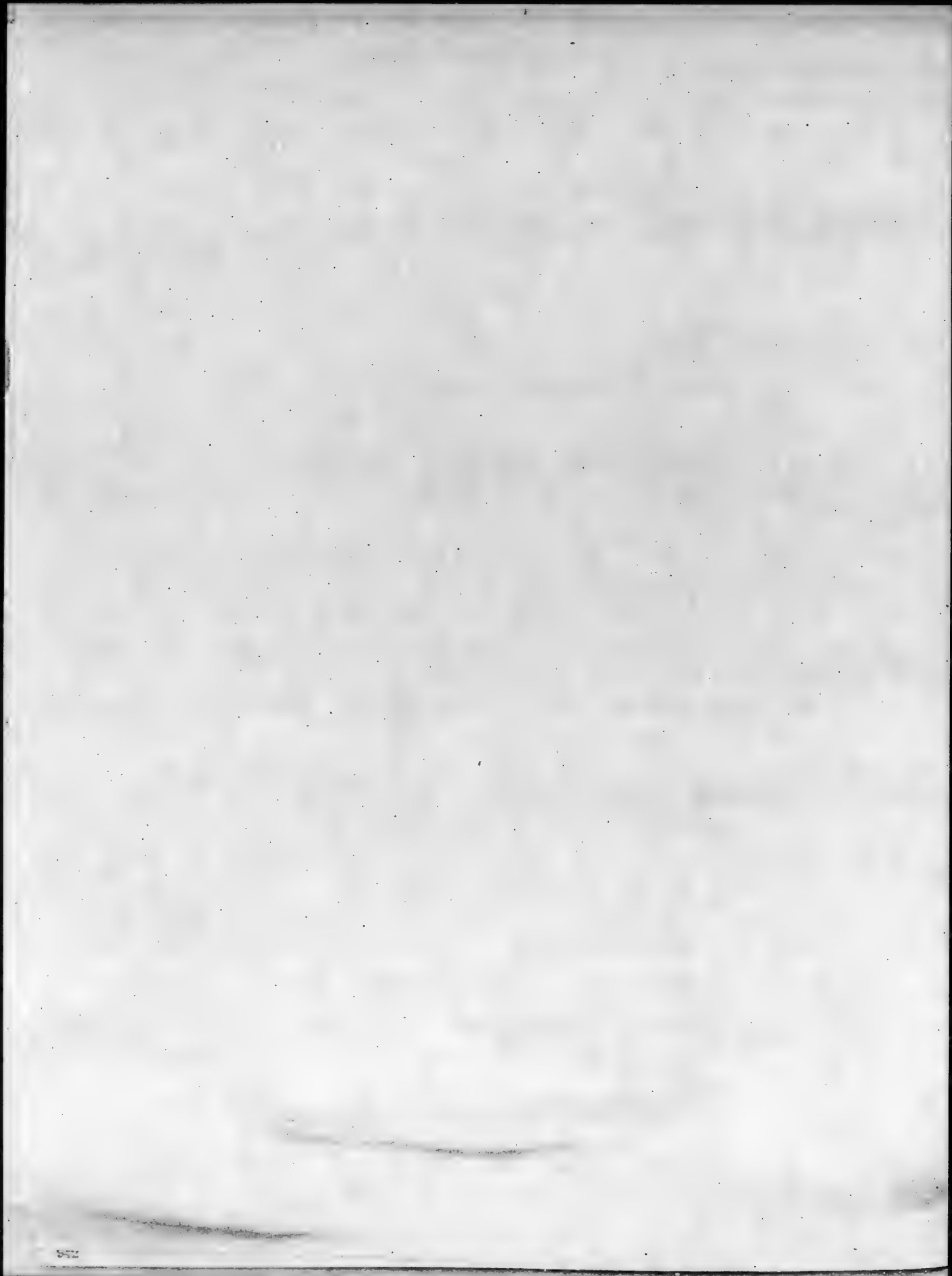
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Received December 28, 1952

Chair of General and Inorganic Chemistry
Kiev Polytechnic Institute Awarded the
Order of Lenin

• See Consultants Bureau Translation, page 1975.



CRYSTALLIZATION OF THREE-COMPONENT SYSTEMS WITH IMMISCIBLE LIQUID PHASES

F. S. Menshchikov

The question of the character of the distribution of the conoids in the region of immiscibility is of principal importance from the point of view of showing the distribution of the components into the conjugate liquid phases, as well as from the general theory of crystallization of monotectics. The material available in the literature on the determination of compositions of two conjugate liquid phases over wide intervals is extremely small, and is related mainly, to ternary systems with disruption in the solubility of one of the binary systems.

D. N. Tarasenkov, in a series of publications [1], first paid attention to the character of the form of the conoids and came to the conclusion that, in ternary systems having a disruption of solubility of the components only in one binary system, the continuation lines of all conoids intersect at one point lying on the continuation of one of the sides of the concentration triangle. In the case of such systems where there is a single region of immiscibility for two binary systems, the continuation lines of all conoids intersect at one of the apexes of the concentration triangle (Fig. 1). Up to now, D. N. Tarasenkov's conclusions have not been discussed in the literature even though they are of probable practical and theoretical interest.

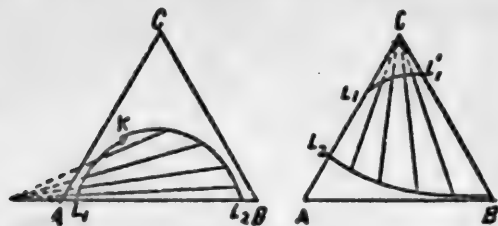


Fig. 1. Scheme for the distribution of conoids in the region of immiscibility according to D. N. Tarasenkov's hypothesis. k) Critical point of immiscibility; L_1 and L_2) first and second liquid layers.

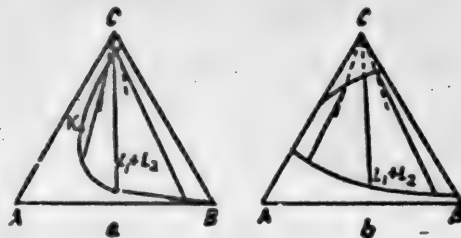


Fig. 2. Method of determining irregularity of the conoids k) Critical point of immiscibility; L_1 and L_2 , first and second layers.

The author of this communication does not share D. N. Tarasenkov's view. It is clearly apparent from the material given in his papers that the abscissa of the intersection points of the continuation lines of the conoids have various values. Although the author correctly recognizes that there were large experimental errors for the calculation of the abscissa of the intersection of the continuation lines of the conoids, the experimental material given by him does allow that the conclusion made be considered completely proved. In addition, D. N. Tarasenkov's conclusions place defined limits on certain systems during crystallization. These limits are not explained by any theoretical principles and are opposed to the experimental material obtained by the authors.

The binary homogenous system in which the immiscibility does not occur, was called by R. V. Mertsilin the prevailing [2], since the reaction of components of the system frequently determines the character of the phenomena occurring in the given ternary system (Systems A-B, Fig. 2a). The second homogenous system in which the critical point is shifted onto separate isotherms, is called the supplementary (Systems A-C, Fig. 2a).

The character of the distribution of the conoids in the region of immiscibility is always such that they form clusters of straight lines radiating like a fan in the direction of the prevalent system. If, from the apex of the concentration triangle signifying the third component (not entering into the binary prevalent system), a series of rays are constructed going up to the region of immiscibility, then, generally speaking, the conoids can be found in various positions relative to these rays. Some conoids will diverge to the right of these rays, others to the left. Because of this, conoids of the right direction and those of the left are differentiated. If the conoids coincide accurately with the direction of the rays, then the direction is zero (Fig. 2b).

R. V. Mertslin proposed that "in the presence of a single region of immiscibility the direction of the conoids will also be single formed, and at the same time, if the subprevailing system occupies the right side of the composition triangle, then the direction of the conoids will be left, as well as the converse of the above" [2]. It must be mentioned that Mertslin's rule for systems in which immiscibility arises in two binary systems almost completely does not agree with Tarasenkov's rule, and therefore does not include those limitations in the behavior of systems during crystallization, which was previously discussed above.

The author's investigation had the following aims 1) to determine which of the two rules are correct for conoids of a two phase liquid state in ternary systems; 2) to determine whether R. V. Mertslin's or D. N. Tarasenkov's rule applies to limited conoids, i.e., to the isothermal lines of the primary crystallization from a two phase liquid state.

A solution of this problem will make it possible to go into a theoretical examination of the behavior of certain systems during crystallization. For this investigation, such systems were chosen in which reactions between the components did not lead to the formation of chemical compounds and solid solutions. Only three systems were studied: epichlorohydrin-toluene-water, phenol-naphthalene-water, and phenol-water-benzoic acid. A single region of immiscibility common for the two binary systems existed. The method of sectioning was used for the investigation of the distribution of conoids. The refractive index of one of the liquids and the crystallization point of one of the components were used as the properties to measure.

The substances used for these systems had the following characteristics: pure benzoic acid with m.p. 121.8°; phenol, redistilled at 181-181.5° and having an m.p. 41.8°; naphthalene, twice purified by sublimation, with m.p. 80.1°. Pure preparations of epichlorohydrin and toluene were not subjected to further purification.

System Epichlorohydrin-Toluene-Water. An Abbe refractometer was used for the investigation of this system. The procedure of the investigation consisted of the measurement of the refractive index of the epichlorohydrin-toluene layer, and the construction of a series of conodes passing through concentration points corresponding to composition points of equal refractive index. For this purpose, 4 sections, characterized by the following amounts of toluene (in %) in the initial binary mixture with epichlorohydrin were chosen: 87.28, 55.33, 31.80, 6.94.

A series of ternary mixtures with differing amounts of water was synthesized based upon these binary (homogeneous) mixtures. The ternary mixtures were thoroughly shaken for 15 minutes and then placed in a thermostat for 24 hours at 25°. The results obtained are given in Fig. 3. The character of the curves obtained showed rather conclusively that the above rule of D. N. Tarasenkov was untrue. Actually, if the conoid continuations intersected at an apex of the concentration triangle (in this case at the apex corresponding to water—Fig. 4), then a gradual increase

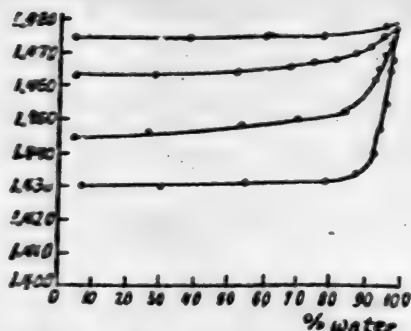


Fig. 3. Change in refractive index of the epichlorohydrin-toluene liquid phase in relation to the concentration of water in the ternary mixture.

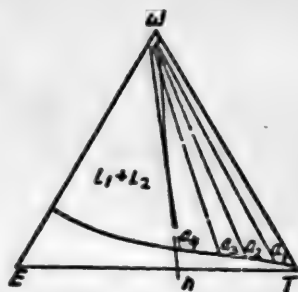


Fig. 4. Schematic diagram of the system epichlorohydrin-toluene-water showing the character of the change in composition of one of the liquid phases in the section W-n.

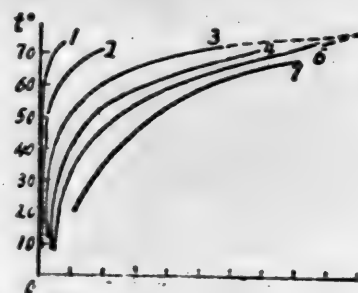


Fig. 5. Curve of the temperatures of beginning of formation of naphthalene crystals.

in the total concentration of water in the ternary system should not be reflected in the quantitative ratio of the components in the conjugate liquid phases, and the refractive index must remain unchanged. The observed change in refractive index indicated that the conoids do not have a zero direction; for this reason any of the sections

chosen intersect a series of conoids. In order to determine the character of the distribution of conoids the chosen sections were placed on the concentration triangle, and the concentration corresponding to equal refractive index values were found on these lines. A series of straight lines coinciding with the conoid directions were found by connecting the concentration points. In all, five of such lines were constructed conoids corresponding to the following refractive indices: 1.4770; 1.4745; 1.4635; 1.4500; 1.4445. Continuing these lines until intersection with the toluene-water side of the concentration triangle, abscissas with the following values were obtained graphically, -19.0; -15.4; -3.8; -2.9; -2.6. The value of the abscissas corresponded to conoids distributed in order of removal from the binary system toluene-water.

Let us now examine to what extent the general character of the distribution of the conoids formed corresponded to the observed changes of the refractive index. In order to show this more clearly, the diagram of the system studied is shown schematically on Fig. 4, in which E, T, and W indicate epichlorohydrin, toluene, and water respectively. The scheme shows the region of immiscibility with a series of conoids the distribution of which qualitatively coincides with those found. With such a distribution of conoids, the section line W-n intersects at the beginning of the conoid in which the composition of the epichlorohydrin-toluene liquid phase corresponds to point a_1 . It is further apparent from the diagram that the composition of this liquid phase will change correspondingly to points a_2 , a_3 , and a_4 , respectively. The closer the section line W-n approaches the apex W, the more sharply the composition of the liquid phase will change: the relative amount of toluene in it increases, and the amount of epichlorohydrin and water decreases. This conclusion agrees fully with the fact that the solubility of epichlorohydrin is considerably greater in water. For this reason, a greater amount of epichlorohydrin must go into the water layer with the increase of the percent water in the whole ternary system, increasing, in this manner, the relative amount of toluene in the epichlorohydrin-toluene layer. If, finally, it is kept in mind that all of the components used, toluene possesses the greatest refractive index, then it becomes very clear that the character of the change in refractive index with the percent water content curves obtained (Fig. 3) agrees completely with that of the distribution of conoids found in the region of immiscibility.

Based on the fact that the mutual solubility of epichlorohydrin in water is greater than in toluene and water, the binary system epichlorohydrin-water can be considered as the subprevailing. Assuming the binary systems to be in such positions as are shown on Fig. 4, it can easily be considered that the character of the distribution of conoids found in the region of immiscibility is in complete accord with R. V. Mertalin's rule.

It must be mentioned that, even though the term "right direction", or "left direction" is purely conditional, the fact of the deviation of conoids from the zero direction is itself very important.

System Phenol-Naphthalene-Water. Timmermans [3], Bantaric and Nabor [4] partially investigated this system, but, since the results of these authors were obtained by scattered experiments, a more complete investigation had to be undertaken. According to literature data and the results of the measurements taken by the authors, the binary systems entering into the given ternary systems having the following characteristics:

1) System phenol-water [5] has a region of interruption of solubility with an upper critical point corresponding to 65.8° the three phased monotectic point is equal to 1.6°, the eutectic composition corresponds to a mixture containing 6.8% of phenol, and the eutectic point is equal to -1.3°.

2) In the system naphthalene-water, the mutual solubility in the studied temperature interval is so small that it is practically impossible to establish the composition and eutectic point. The upper critical temperature of the region of immiscibility was not determined since it was sufficient to know that the critical point of this system was a considerably higher temperature than that in the system phenol-water. The monotectic point was equal to 78.4°.

3) According to Hatcher and Skirrow's [6] data, the eutectic in the system phenol-naphthalene lies at 29.8° and contains 84% of phenol. In order to study the phase composition of the system, the concentration triangle of the composition Ph-N-W (phenol-naphthalene-water) was sectioned with rays having their origin in the various concentration points of the binary system Ph-W and going to the apex N of the triangle. In all, seven sections were studied characterized by phenol contents (in %) in the binary mixture Ph-W: 4.9, 10.1, 25.0, 50.0, 64.7, 75.0, 90.4.

A ternary mixture was synthesized based on these binary mixtures, and the initial starting mixture was heated to a temperature at which complete homogenization of the solution occurred.

Working with these ternary systems, the following aims were sought: a) to determine the surface of crystallization of the three phased monotectic in order to make possible the construction of several limited conoids;

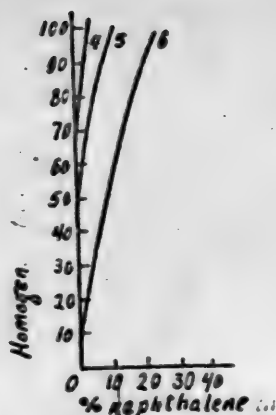


Fig. 6. Polythermic immiscibility curves.

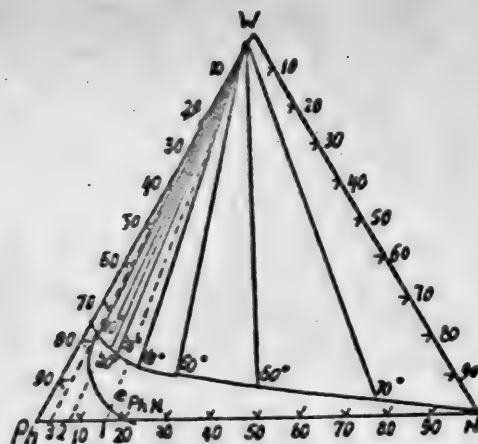


Fig. 7. Projection of the polytherms of the structural diagram of phenol-water-naphthalene showing the positions of the limited conoids and those of the sections chosen (dotted lines 1, 2, and 3).

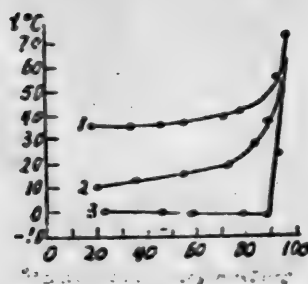


Fig. 8. Change of crystallization point in the verifying sections 1, 2, and 3.

TABLE 1

Conoid temperature (°C)	Section 3		Section 6		X
	c_1	a_1	c_2	a_2	
73	55.00	11.25	81.25	14.25	-42.5
70	43.30	14.17	72.10	20.9	-17.33
60	18.40	20.4	42.80	42.9	-3.27
50	8.00	23.0	23.8	57.0	-2.68
40	4.50	23.9	13.6	64.8	-0.81
30	3.00	24.2	9.0	68.5	-0.27
20	2.40	24.4	7.3	69.5	-0.18
10	1.00	24.4	5.0	71.2	-0.17

with the binodal curve corresponding to the given isotherm, seven limited conoids were obtained. In order to quantitatively characterize the distribution of limited conoids in the region of immiscibility, D. N. Tarasenkova's equation $X = \frac{a_2 c_1 - a_1 c_2}{a_2 - a_1}$ was used where X is the abscissa points of conoid lines with the continuation of one side of the concentration triangle, and $a_1 c_1$ and $a_2 c_2$, the coordinates of the two conjugate liquid phases. Since the composition of the conjugate liquid phases was not determined directly during this method of investigation, two points lying on sections 3 and 6 were used for the calculation of the abscissas for each of the conoids. The concentration of phenol was used for coordinates a_1 and a_2 and the concentration of naphthalene for c_1 and c_2 . The numerical material for these calculations is given in Table 1.

The calculated values of the abscissas of intersection points of conoid lines with the continuation of the naphthalene-water side of the triangle show that: 1) the continuation lines of limited conoids do not intersect at the apex of the concentration triangle, and 2) at the corresponding distributions of the binary systems, all of the conoids have a right direction, which corresponds to R. V. Mertsin's rule.

In order to prove the character obtained for the distribution of the conoids, 3 more sections were investigated which had their start in the binary system phenol-naphthalene and are characterized by the following phenol contents (%): 85.0, 93.0, 97.0.

For a better description and subsequent conclusion, the projection of the polytherms of the structural diagrams of Ph-W-N is given in Fig. 7, in which are shown the positions of the limited conoids found, and the lines of the chosen sections (dotted lines 1, 2, and 3). In accordance with the position of the limited conoids in these sections, approximately the same form for the curves of the variation of crystallization point of three-phased monotectic with the total weight

b) to construct polythermic curves in the region of the two-phased liquid state for the chosen sections using the well known polythermic method of Alekseev

[7] in order to construct a binary curve of the region of immiscibility on the separate isotherms.

On the basis of the graphic material obtained, curves of the start of the primary separation of naphthalene crystals from the two-phased liquid state, which corresponded to sections 1, 2, 3, 4, 6, and 7, (Fig. 5), as well as a polythermic curve of the region of immiscibility corresponding to sections 4, 5, and 6 (Fig. 6) were constructed. In order to construct a series of limited conoids, the composition points were determined on the graphs corresponding to 70, 60, 50, 40, 30, 10°, and then placed on the corresponding rays of sections 1, 2, 3, 4, and 6. Joining the points with straight lines and continuing them to intersection

percent of water in the ternary system must be expected (Fig. 3). Actually, the section lines will intersect a series of conoids corresponding to higher temperatures in relation to the total concentration of water; the closer the figurative point of composition approaches the apex W, the greater must be the increase of the crystallization point of the monotectic in the defined concentration interval.

Such a variation of temperature of the monotectic curve indicates the fact that, in relation to the increase of the concentration of water in the ternary system, because of the large mutual solubility of phenol and water, the phenol-naphthalene layer will be more and more depleted of phenol. Conversely, the relative concentration of naphthalene will increase and therefore, the crystallization point of naphthalene will increase.

Complete polythermic diagrams of the sections studied are not given here; only the relation of the crystallization point of the monotectic to the total concentration of water in the system will be shown. On Fig. 8 it is clearly apparent that the expected temperature variation curves for sections 1 and 2 are proved. The lower curve, corresponding to section 3, is different in form, as well as in character of the monotectic process from the first two, but this difference does not disprove but confirms the character of the distribution of conoids. From the diagrams in Fig. 7, it is apparent that the line of section 3 passes to the left of the conoids upon which the four-phased monotectic process is realized. Therefore, (and this is confirmed by direct observation) initially, the three-phased monotectic exists on this line with phenol crystals. Then, with the concentration of water of about 87%, the section line intersects the conoid of the four-phased monotectic (-0.65°) and enters into the region of the monotectic with naphthalene crystals.

Although the positions of the conoids, distributed in the region of the three-phased monotectic with phenol crystals is, practically, very difficult to determine, since the temperature interval between the monotectic in the system Ph-W and the four-phased monotectic is only equal to 2.2° , nevertheless, it can be concluded from the diagram of section 3 that there exists one direction for the conoids in the entire system.

System Phenol-Water-Benzic Acid. According to the literature data [6,8], the upper critical temperature of immiscibility of the binary system benzoic acid-water is equal to 115.5° ; the three-phased monotectic point is equal to 95° . The eutectic point in the system phenol-benzoic acid is equal to 31° and corresponds to a composition containing 82.5% phenol.

In order to show the character of the crystallization surface of the three-phased monotectic in the system phenol-water-benzoic acid (Ph-W-B) at $20-80^\circ$, 7 sections were investigated. The lines of these sections originated at various concentration points of the binary system Ph-W and passed into the apex B of the concentration triangle Ph-W-B. The phenol content (in %) of the binary mixture (Ph-W) was the following: 3.95, 9.6, 15.1, 25.0, 50.0, 62.6, 75.6.

Ternary mixtures with varying amounts of benzoic acid were synthesized on the basis of these binary mixtures of Ph-W, and then the immiscibility point and the temperature of separation of the first benzoic acid crystals from the two-phased liquid state were measured. The results of these measurements are given in Figs. 9 and 10.

Using the above reported method, a series of limited conoids corresponding to temperatures: $80, 70, 60, 50, 40, 30$, and 20° were constructed, and the intersection points of the conoids with the continuation of the side W-B of the concentration triangle Ph-W-B on the abscissa was calculated. Necessary data for this calculation are given in Table 2. Here c_1 and c_2 are the concentrations of benzoic acid used in sections 2 and 6 and a_1 and a_2 the concentration of phenol in these sections.

TABLE 2

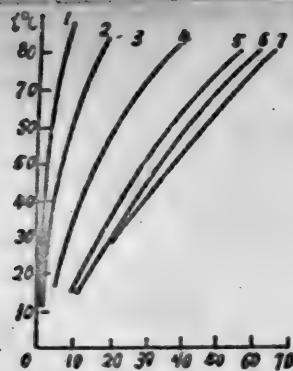
Conoid temperature ($^\circ\text{C}$)	Section 2		Section 6		X
	c_1	a_1	c_2	a_2	
80	16.5	8.0	60.1	25.0	-4.01
70	11.5	8.5	49.0	31.9	-2.12
60	8.3	8.76	40.0	37.5	-1.36
50	6.0	9.0	32.8	43.2	-1.05
40	4.4	9.17	26.0	46.15	-0.95
30	3.0	3.31	19.0	50.63	-0.60
20	2.0	9.4	14.0	53.75	-0.54

It is apparent from Table 2 that the conoids do not intersect at the apex of the concentration triangle, and that the character of the distribution of the conoids is the same as in the previously reported systems.

It must be mentioned that, above 65.8° , the region of immiscibility does not reach the binary system Ph-W. This fact does not introduce any important changes in the character of the distribution of the limited conoids.

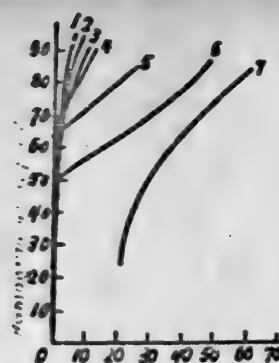
In order to prove the correctness of the distribution found for the conoids, 2 more sections originating in the binary system Ph-B and going to the apex W of the concentration triangle were investigated. The starting binary mixture with benzoic acid had the following phenol content (in %): 82 and 90.

The dotted lines in Fig. 11, designated by the numbers 1 and 2, show the position of the confirming sections. The region of immiscibility is not shown on the diagram, while the limited conoids are bounded by sections 1-7. The eighth



% Benzoic acid in the ternary system

Fig. 9. Curve of the temperature of the start of crystallization of benzoic acid.



% Benzoic acid in the ternary mixture

Fig. 10. Polythermic immiscibility curves.

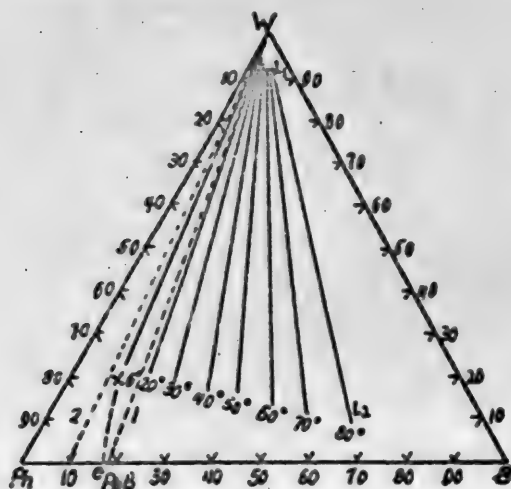
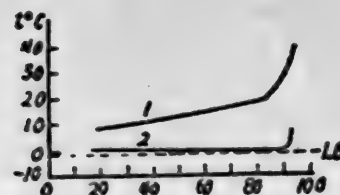


Fig. 11. Distribution of limited conoids in the region of immiscibility and the position of verifying sections 1 and 2.



% water in the ternary mixture.

Fig. 12. Variation of the crystallization point in the verifying sections 1 and 2.

conoid: corresponding to -1.6° , is the one upon which the four-phased monotectic process exists.

Even from the diagrams in Fig. 11, it is apparent that section 1 line intersects by means of its continuation from the side Ph-B to the apex W, the conoid corresponding to 20° , and then a series of other conoids with higher crystallization points. Therefore, the curve of the variation of crystallization point of the

monotectic with the percent water content in the ternary mixture must have a form analogous to curves 1 and 2 on Fig. 8 in this section.

Section line 2 passes initially through the region of crystallization of the monotectic with phenol crystals, and only at concentrations of water in the ternary mixture equal to 92%, intersects the four-phased monotectic conoid. The results of the measurements for the chosen sections given in Fig. 12, confirm the previous statements.

The fact that the curve of the monotectic with phenol crystals (section 2) falls in the direction of lower temperatures indicates that, in this system, in a similar manner to the system phenol-water-naphthalene, a single direction for the limited conoids exists.

The relatively small rise of the curve in the direction of higher temperatures with these sections, is explained by the fact that the region of immiscibility is less developed in this system than in that of phenol-water-naphthalene. For this reason, conoids corresponding to higher temperatures are intersected sooner by the binodal curve than by the section lines.

This character of distribution of conoids makes it possible to theoretically predict the qualitative changes in conjugate phases and the behavior of certain systems during crystallizations for any system in which chemical compounds or solid solutions do not arise.

SUMMARY

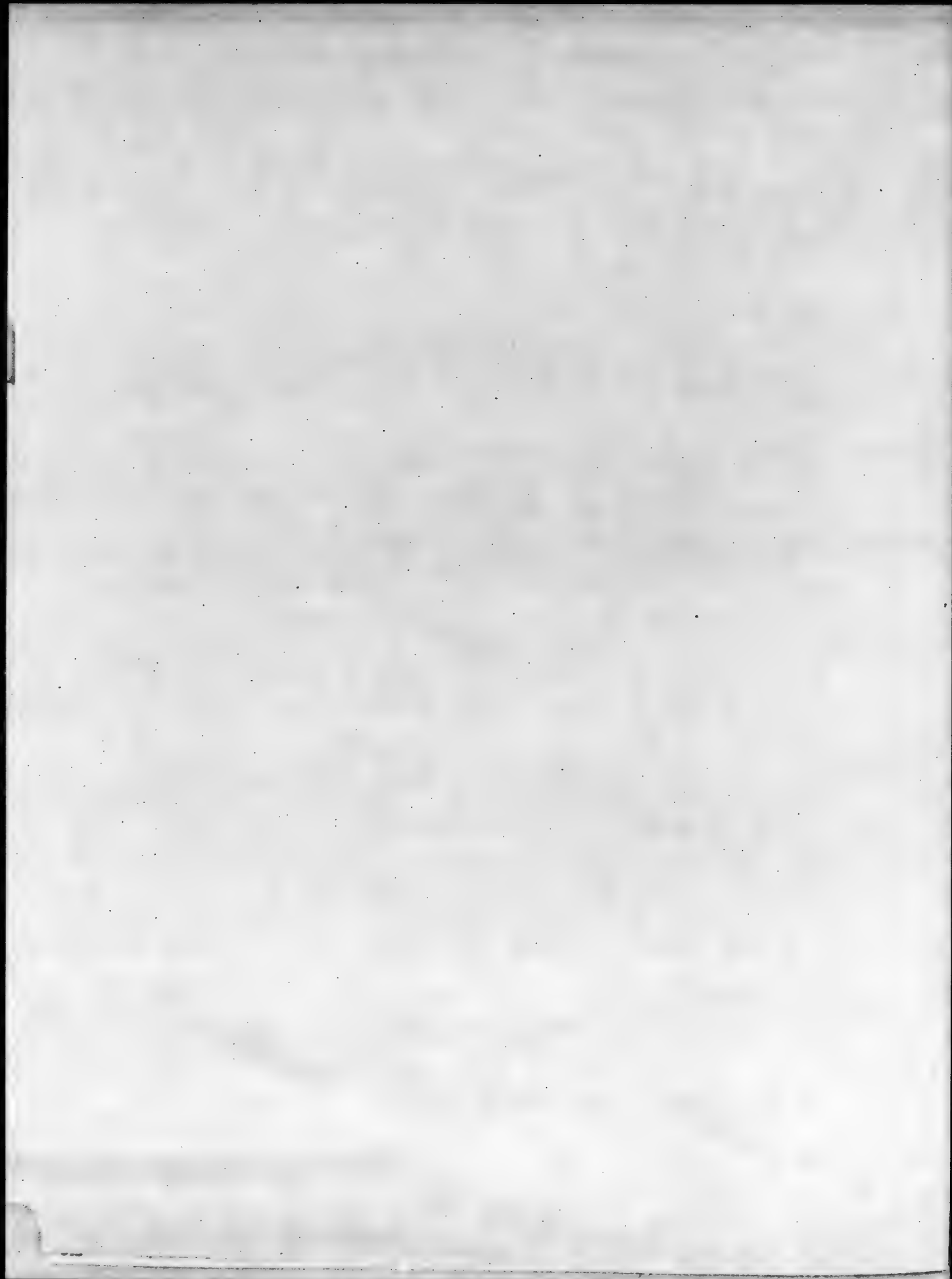
1. The theoretical conclusions of R.V. Mertsin on the single direction of conoids in the ternary system with a single region of immiscibility for the two binary systems were proved correct for the systems studied: epichlorohydrin-toluene-water, phenol-naphthalene-water, and phenol-water-benzoic acid.
2. It was shown that the character of the distribution of conoids of the two phased liquid state is retained up to the crystallization point, i.e., it embraces the limited conoids which are iso thermal crystallization lines in the region of immiscibility.
3. The hypothesis of D.N. Tarasenkov on the joining of the continuation lines of the conoids at one of the apexes of the concentration triangle was disproved.
4. The results obtained gave a basis for the general qualitative evaluation of structural diagrams and enable methods for the crystallization of certain ternary systems to be determined.

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Received April 14, 1951.



COMPLEX COMPOUNDS OF NICKEL WITH DIMETHYLGLYOXIME

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The reaction of the nickel ion with dimethylglyoxime has been known for a long time, but up to now, the question of the structure of the soluble complex compound obtained by the reaction of nickel with dimethylglyoxime in alkaline medium remains unanswered. Feigl [1] considers that the soluble complex is a compound of dimethylglyoxime with tetravalent nickel.

Hooreman [2] states that dimethylglyoxime gives two colored complexes with tetravalent nickel. In one the ratio of nickel to dimethylglyoxime is equal to 1:2, in the other, 1:4.

Another view is held by Babko [3]. He believes that nickel is divalent in this complex and is combined with an unstable product of the oxidation of dimethylglyoxime. The composition of the complex corresponds to a ratio of nickel to dimethylglyoxime equal to 1:2, for a small excess of the oxidizing agent, and 1:3 for a large excess.

It was observed that, upon mixing solutions of nickel salts with those of dimethylglyoxime in the presence of concentrated ammonia, no precipitate is formed, and the solution is gradually colored red. A colored complex compound is formed, it is believed, the study of whose properties is of interest from a theoretical as well as from a practical viewpoint.

The system nickel sulfate-dimethylglyoxime-aqueous ammonia solution was studied. The method of Ostromyslensky-Dzhob, i.e., the study of the mixture of solutions of nickel sulfate and dimethylglyoxime of identical polarity under various volume ratios at a constant total volume, could be used to determine the composition of the colored compound. But this method can only give a one sided characterization of the system, since it detects the existence of only one complex compound.

Babko [5] further developed the method for the investigation of solutions of complex compounds and offered to study more widely the properties of a similar type of multicomponent system. The system investigated can be schematically described in the form of a triangle (Fig. 1). Using Babko's method, the properties of the system were studied by means of sections 1-2, 3-4, and 5-6. The optical density of the mixture was chosen as the property of the system.

EXPERIMENTAL

0.0044 molar solutions of nickel sulfate and dimethylglyoxime were used for the investigation.

During the preparation of the mixture, it was found that the reaction forming the colored complex proceeds with time.

The results of the observation are shown on Fig. 2.

During the first 80 hours the optical density of the solution (the thickness of the absorption layer was 5 cm) increased continually, acquired a maximum, and was constant for the following 60 hours, and then very slowly decreased. All of the subsequent observations were conducted after 4-5 days (100-120 hours).

At first, mixtures with changing concentration of nickel sulfate and dimethylglyoxime and a constant concentration of aqueous ammonia were investigated in series of experiments. Sections of the type 1:2 on Fig. 1 correspond to those. Upon the preparation of mixtures of solutions of nickel sulfate and dimethylglyoxime of various volume ratios, the total volume remained constant. The total molarity of the nickel sulfate and dimethylglyoxime in the experiments was equal to $8.8 \cdot 10^{-4}$ M.

Three series of mixtures were investigated. In each series, the concentration of ammonia was changed. In the first series, the total molarity of the ammonia was 3.25, in the second, 4.37, and in the third, 5.58. Within five days after the preparation of the mixture, the optical density of the solution was measured on a Moskin photocolorimeter with yellow filters. The variation of the optical density with the ratio of the volumes of nickel sulfate and dimethylglyoxime is described on Fig. 3 by three curves. All of the curves have a maximum at a ratio

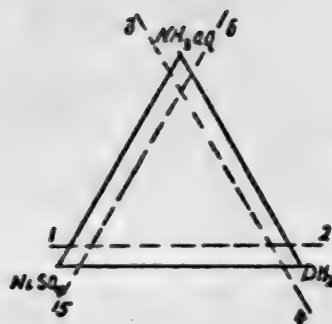


Fig. 1. Scheme of the directions of the sections in the system nickel sulfate-dimethylglyoxime-aqueous ammonia solution.

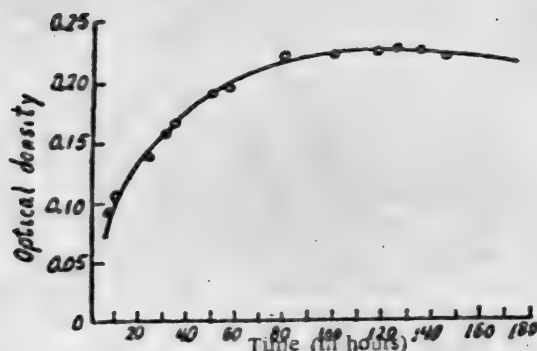


Fig. 2. Curve of the change in color of the complex with time.

of volumes of nickel sulfate and dimethylglyoxime, equal to 1.3, which corresponds to the same ratio for the number of molecules.

Then a mixture with a constant concentration of nickel sulfate ($8.8 \cdot 10^{-5}$ moles) and a changing concentration of dimethylglyoxime (from $2.64 \cdot 10^{-4}$ to $1.3 \cdot 10^{-3}$ moles), was investigated, corresponding to section 3-4 on Fig. 1. The concentration of ammonia in all of these experiments was constant and was equal to 3.36 moles. The variation of the optical density of the solution with the concentration of dimethylglyoxime for this case is shown on Fig. 4.

The system nickel sulfate-dimethylglyoxime-aqueous ammonia solution was also investigated at section 5-6 (Fig. 1) in this case, the concentration of dimethylglyoxime was kept constant ($8.8 \cdot 10^{-5}$ moles), and the concentration of nickel sulfate was changed (from $4.4 \cdot 10^{-5}$ to $3.52 \cdot 10^{-4}$ moles). The concentration of ammonia in all experiments was 3.36 moles. The results of the measurement of the optical density of these solutions is shown on Fig. 5.

DISCUSSION OF RESULTS

The optical data obtained by the investigation of the systems of nickel sulfate-dimethylglyoxime-aqueous ammonia made is possible to make a suggestion on the nature of the colored complex which formed. According to the authors, the compound of nickel and dimethylglyoxime in ammoniacal medium, is the product of the reaction of dimethylglyoxime, bivalent nickel, and the oxygen of the air which is the oxidizing agent. This is confirmed by experiments conducted with solutions prepared with redistilled water saturated with nitrogen. Such solutions, sealed in ampoules, remained practically colorless even on prolonged standing. When these ampoules were opened the solution colored rapidly, and in certain of these where the concentration of nickel was high, a precipitate formed. Apparently, the oxygen of the air oxidizes the dimethylglyoxime, and the latter reacts with bivalent nickel.

The properties of the solutions of the colored complex compound of nickel with dimethylglyoxime reported is essentially different from those reported by Feigl [1], since, for example, by the oxidation of the solutions obtained, neither a red brown precipitate nor iodine from potassium iodide solutions was formed.

The formation of the colored complex compound, as was stated above, does not occur with the complete absence of oxygen in the water and occurs in the presence of even small amounts of oxygen after some time; for this reason the above reaction may be used to detect dissolved oxygen in water and in aqueous solutions.

The curve in Fig. 2 shows the change of the optical density of the mixture containing nickel sulfate, dimethylglyoxime, and ammonia with the time. The optical density passes through very flat maximum and then decreases which indicates the simultaneous occurrence of at least 2 processes in the system, the formation of the complex compound and very slowly, its decomposition. It must be mentioned that the solutions keep their color even after several months.

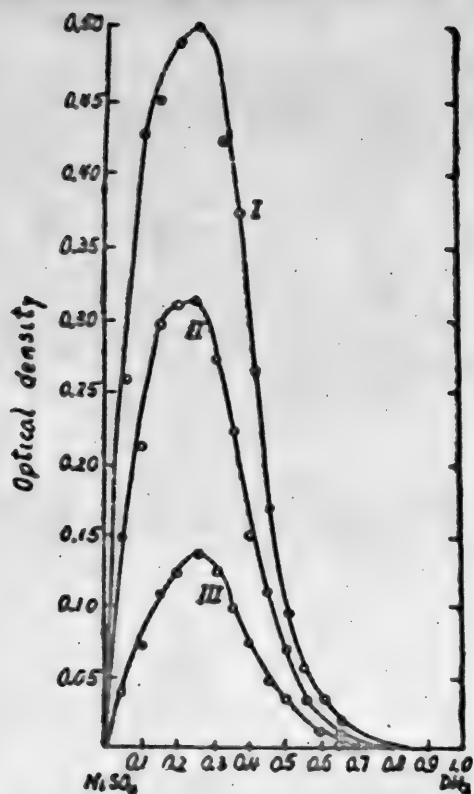


Fig. 3. Volume ratio of solutions of nickel sulfate and dimethylglyoxime according to section 1-2 and the optical density.

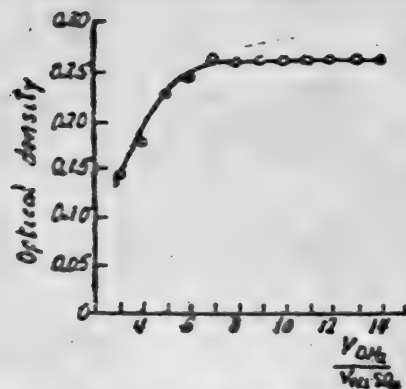


Fig. 4. Variation of the optical density with the concentration of dimethylglyoxime according to section 3-4.

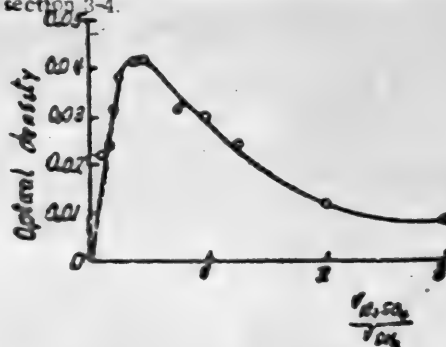


Fig. 5. Change in the optical density of the solution of the system nickel sulfate-dimethylglyoxime according to section 5-6.

On curves I, II, III (Fig. 3) for the system nickel sulfate dimethylglyoxime-ammonia, a maximum optical density can be found at ratios of nickel sulfate to dimethylglyoxime equal to 1:3, which apparently, corresponds to the composition of the compound formed. The curves obtained are not symmetrical. Branches of the curve to the right of the maximum pass considerably more abruptly downward than those to the left of it, and at ratios of the number of molecules equal to 1:1, a clear inflexion can be seen on the curve. Such a form of the curve, indicates, according to the authors, the existence in addition to the colored complex (with a molar ratio of the components, 1:3), another, colorless one (with a suggested ratio of the reacting components 1:1). The same conclusion, as it will be shown below, is arrived at by the study of the systems with a constant concentration of dimethylglyoxime.

From the curves I, II, III placed on Fig. 3, it is apparent that, with the change of the concentration of the ammonia, the position of the maximum does not change, only its height changes. The highest maximum corresponds to a mixture in which the concentration of ammonia is 3.52 molar, the lowest maximum, with a concentration of 5.58 molarity. Therefore, with the increase of the concentration of ammonia, the degree of dissociation of the complex increases. This phenomenon can be explained if it is assumed that the following equilibrium occurs in the solution:



where DH^+ is the oxidized form of dimethylglyoxime. Supplementary proof of the existence of such an equilibrium in the system studied will be given below.

Upon keeping the initial concentration of nickel sulfate constant and continually increasing the concentration of dimethylglyoxime (in ammonia solution), the curve of the optical density first rises sharply, then becomes almost parallel to the abscissas, and approaches a definite value of the optical density (Fig. 4). This value of the optical density corresponds to practically complete conversion of the nickel salt to the complex compound, equilibrium (1)

is practically completely shifted to the right.

The compounds formed in the system are found in the partially dissociated state. If the dissociation of the compounds were insignificant, then the graph, shown on Fig. 4, would have been a broken line with an inflexion occurring at the composition of the complex compound.

Nevertheless, the compounds of nickel with dimethylglyoxime possess a sufficiently great stability, since if an extensive dissociation were present, there would have been no horizontal branch found on Graph 4.

The molar extinction coefficient of the compound formed was calculated from the determined values of the optical density (Fig. 4). It was assumed that practically all of the nickel sulfate found in the solution had been converted into the complex compound. By investigating the graph in Fig. 4, the ratio of nickel to dimethylglyoxime in the colored complex can once more be verified. The "logarithmic graph" method was used for this purpose. By substituting the concentrations of the reaction components from the experimental data into the equilibrium equation expressing the constants of the reaction forming the colored complex, we obtain:

$$\frac{\alpha D C_{\text{Ni}}^0}{(C_{\text{Ni}}^0 - \alpha D)(C_{\text{DH}}^0 - 3\alpha D)^3} = K_e$$

where D is the optical density; $\alpha = \frac{1}{E}$ (E is the molar extinction coefficient for the complex compound solution) l is the thickness of the absorption layer; C_{DH}^0 , C_{Ni}^0 and $C_{\text{NH}_3}^0$, the initial concentrations of dimethylglyoxime, nickel, and ammonia.

The product αD is equal to the concentration of the colored complex in the solution.

By rearranging the expression for the equilibrium constants and transforming it into logarithms, a relation is obtained expressed by a straight line, if the abscissas are made to correspond to the logarithmic ratio of the concentration of the colored complex to the equilibrium concentration of nickel and the equilibrium concentration of dimethylglyoxime, to the ordinates.

$$\log \frac{\alpha D}{C_{\text{Ni}}^0 - \alpha D} = \log K_e - 6 \log C_{\text{NH}_3}^0 + 3 \log (C_{\text{DH}}^0 - 3\alpha D).$$

The tangent of the angle of inclination characterizes the coordination number which was found to be equal to 3 (Fig. 6).

Therefore, the same result for the composition of the complex is found by the logarithmic graph method as by Ostromyslenky-Dzhob's method.

The section, cut off by the straight line on the ordinates at an equilibrium concentration of dimethylglyoxime equal to 1 molar, is directly related to the value of the equilibrium constant. The value of the logarithm of the equilibrium constant calculated from the data given in Fig. 6, was found to be equal to 14.8. This value was confirmed by the calculation of the equilibrium constant from the optical data from mixtures with varying concentrations of dimethylglyoxime and nickel sulfate (with different concentrations of ammonia) (Fig. 3).

The values ≈ 14.1 and 14.9 are obtained in this case for the logarithm of the equilibrium constant, which is close to that calculated above.

The instability constant of the colored complex was calculated, which is related to the simple ratio of the equilibrium constant of reaction (1) and the instability constant of the complex ion $\text{Ni}(\text{NH}_3)_6^{2+}$.

$$K_{\text{instability}} = \frac{K_{\text{instability Ni}(\text{NH}_3)_6^{2+}}}{K_e}$$

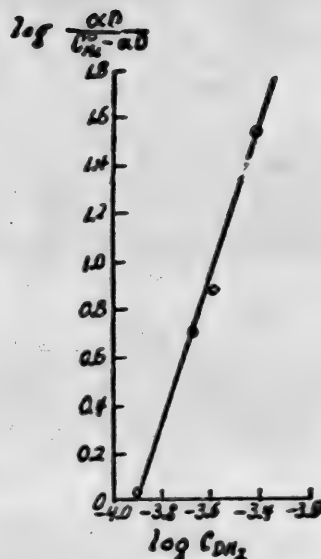


Fig. 6. "Logarithmic graph" of the system.

The instability constant of $\text{Ni}(\text{NH}_3)_6^{2+}$, according to Bjerrum [4], is equal to $1.8 \cdot 10^{-9}$. The instability constant of the colored complex was found to be equal to $3 \cdot 10^{-23}$.

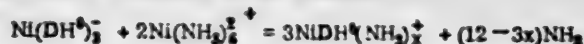
The curve in Fig. 5, expressing the relation of the optical density to the concentration of nickel sulfate (at constant initial concentration of dimethylglyoxime in the solution), shows that the maximum optical density approaches a molar ratio of nickel to dimethylglyoxime equal to 1:3. The following reaction occurs in the solution:



On further increasing the concentration of nickel sulfate the optical density of the solution decreases and approaches zero.

If other complex compounds did not exist in the solution, then the optical density would have remained almost constant. Apparently the excess nickel sulfate reacts with the colored complex and converts it into another uncolored complex with a smaller coordination number.

The reaction occurs, evidently, by the equation:



The composition of the complex compound with a ratio of nickel to dimethylglyoxime of 1:1 was adopted because the compound of nickel and dimethylglyoxime with a ratio of 1:2 is colored. In addition, the position of the inflexion point on the curves in Fig. 3 favors this view.

Therefore, a many sided investigation of the system nickel sulfate-dimethylglyoxime-ammonia leads to the conclusion that at least two complexes are present in the system; one is colored which has a ratio of nickel to dimethylglyoxime equal to 1:3, and the other is colorless with a ratio, evidently, equal to 1:1.

SUMMARY

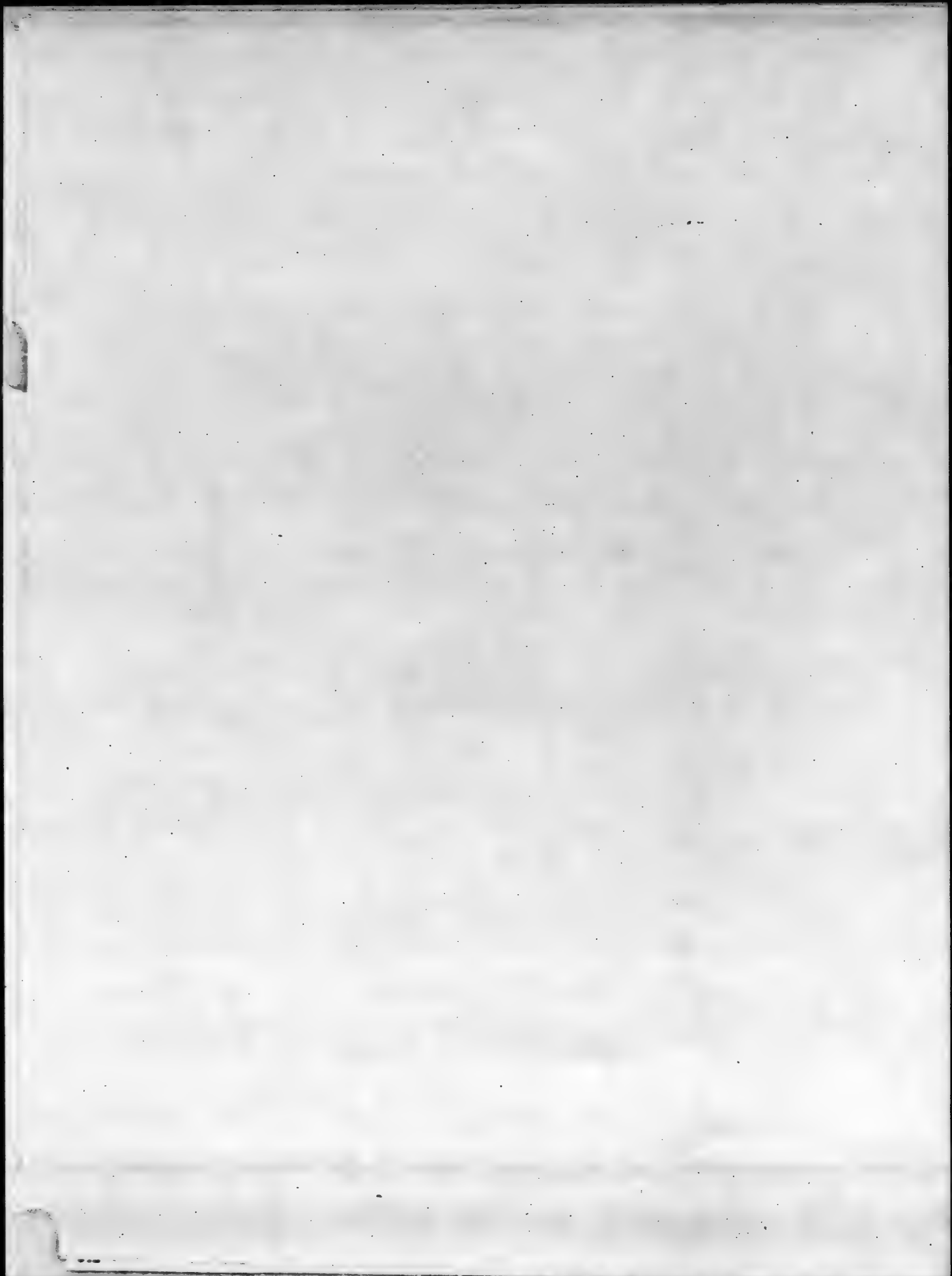
1. The formation of a colored complex was discovered upon the reaction of nickel sulfate with dimethylglyoxime in an ammoniacal medium in the presence of oxygen from the air.
2. The composition of the colored complex was determined by a physico-chemical method of analysis and corresponded to a ratio of nickel to dimethylglyoxime equal to 1:3.
3. The reaction forming the colored complex occurs with time.
4. In addition to the colored complex compound, a colorless one exists in the system with a molar ratio of nickel to dimethylglyoxime equal to 1:1.
5. On the basis of the study of the reaction between the complex compounds formed and the ammonia, the corresponding equilibrium constant and instability constant of the complex compound of nickel with dimethylglyoxime were calculated.

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Received February 10, 1953

The Ivanov Institute of Chemical Technology

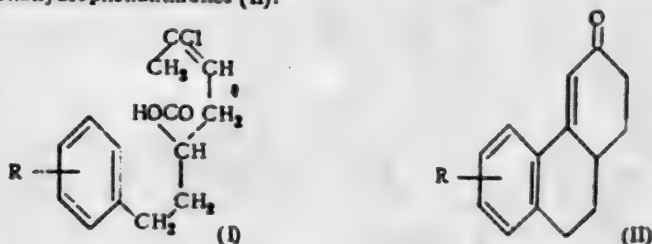


SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

VII. 5- and 7-METHOXY-3-KETO-1,2,3,9,10,10a-HEXAHYDROPHENANTHRENES

G. T. Tatevosyan, P. A. Zagorets and A. G. Vardanyan

Previously, it was shown [1] that sulfuric acid hydrolysis and subsequent double cyclization of substituted γ -phenylbutyric acids with a γ -chlorocrotyl group in the α -position to the carboxyl(*H*) leads to the formation of substituted 3-ketohexahydrophenanthrenes (II):

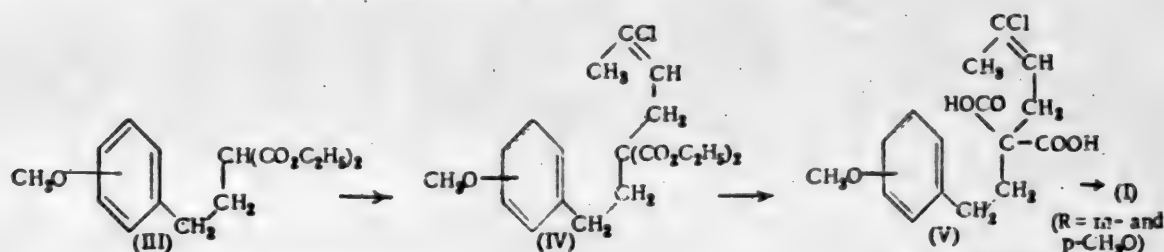


It was also found that the presence and position of a methyl group in the aromatic nucleus of the starting acid did not have any significant effect on the tendency of the acid to cyclize and on the yield of the reaction products [2].

It seemed of interest to investigate the analogous transformation of acids of this series with a methoxyl group in the aromatic nucleus, which is, as is known, a considerably stronger expressed ortho and para orientating substituent than the methyl group.

The expected cyclization products were ketomethoxyhexahydrophenanthrene (II, R = 6- and 7-CH₃O) which in themselves can be of interest as starting substances for the synthesis of compounds related in structure to Doisydolone acid, as well as for the preparation of analgesically active amino derivatives of partially hydrogenated phenanthrene.

The above acids (I, R = *m*- and *p*-CH₃O) were prepared from the corresponding β -anisylethylbromides and 1,3-dichlorobutene-2 by means of the malonic acid via compounds (III), (IV), and (V):



The ability of γ -phenylbutyric acids to intramolecularly acylate depends to a considerable degree on the nature and position of the substituents found in the aromatic nucleus

According to certain literature data [3], γ -(*m*-anisyl)butyric acid (VI, R = *m*-CH₃O) readily undergoes intramolecular acylation and forms 6-methoxytetralone-1 (VII, R = 6-CH₃O) by the action of sulfuric acid and other cyclizing agents:



On the other hand, Krollpfeiffer and Schäfer [4] did not obtain any 7-ethoxytetralone-1 (VII, R = 7-CH₂O) when they tried to cyclize γ -(p-anisyl)butyric acid (VI, R = p-CH₂O) by heating with sulfuric acid; the starting material was completely sulfonated. This substance can not only be explained by the facile sulfonation of the aromatic ring in the starting acid, but also by the deactivating effect of the methoxyl group upon cyclization. The latter view is confirmed by the fact that the same γ -(p-anisyl)butyric acid cyclizes only to an extent of 61.5% [5] by the action of liquid hydrogen fluoride, while the unsubstituted acid (VI, R = H) from tetralone-1 (VII, R = H) in a yield of 92.0% [6] under the same conditions.

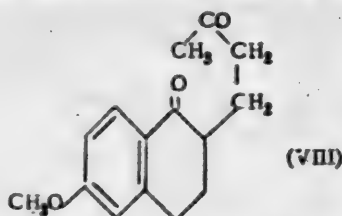
Therefore, the methoxy group, as an ortho-para-orienting substituent, hinders the intramolecular acylation which occurs in the meta position in relation to this group.

From a study of the reported literature data, it was expected that sulfuric acid hydrolysis and cyclization of α -(3-chlorocrotyl)- γ -(m-anisyl)butyric acid (I, R = m-CH₂O) into 3-keto-7-methoxyhexahydrophenanthrene (II, R = 7-CH₂O) would occur smoothly, whereas it could be expected that the complete sulfonation of the isomeric acid (I, R = p-CH₂O) was probable, since both are γ -(p-anisyl)butyric acids substituted in the side chain.

On the other hand, the presence of a substituent in the α -position to the carboxyl group, which favored, according to other observations [7], cyclization of γ -arylbutyric acids, gave a basis for expecting that the intramolecular acylation will occur at comparatively lower temperatures which do not favor sulfonation.

3-Keto-7-methoxyhexahydrophenanthrene (II, R = 7-CH₂O), characterized in the form of 2,4-dinitrophenylhydrazone, was obtained in 57% yield by the reaction of α -(3-chlorocrotyl)- γ -(m-anisyl)butyric acid (I, R = m-CH₂O) with sulfuric acid (d 1.78) at 60-75°.

Under more forcing conditions, the sulfonation of the starting acid was greatly intensified which strongly decreased the yield of tricyclic ketone, while gentler conditions (moderate and shorter heating of the reaction mixture) resulted in a reaction product which was a mixture of the final substance and the bicyclic diketone (VIII) formed as a side product:



A still more sharply expressed separate occurrence of the two stages of cyclization was previously found during the preparation of ketones with the chrysene cyclic system [8]. The intramolecular aldol condensation of the remaining part of the intermediate diketone into the ketomethoxyhexahydrophenanthrene was effected by boiling the mixture obtained with aqueous alkali.

There, the presence of a methoxyl group in the meta position, actually, does not prevent cyclization. Nevertheless it must be mentioned that the yield of the cyclization product (57%) was somewhat lower than the yields obtained with the unsubstituted acid [1] or acids methylated in the aromatic ring of the same series [2] (60-80%), which, evidently, must be explained by comparatively easy sulfonation of the methoxylated aromatic ring.

Upon attempting to cyclize α -(3-chlorocrotyl)- γ -(p-anisyl)butyric acid (I, R = p-CH₂O) with sulfuric acid (d 1.74) at 65-70°, it was almost completely sulfonated, and only a very small amount of a substance which proved

to be 3-keto-6-methoxyhexahydrophenanthrene (II, R=6-CH₃O) could be isolated from the reaction mixture.

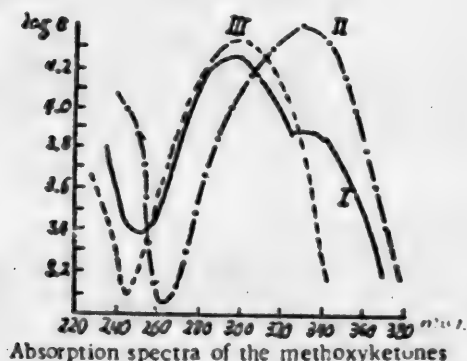
In isolated cases, substituted γ -phenylbutyric acids are cyclized with sulfuric acid at lower temperatures. Thus, V. M. Rodionov and N. N. Suvorov showed [9] that the triethyl ester of α -phenyl- β -benzylethane- α,β,β -tricarboxylic acid readily cyclized into 3,3-dicarbethoxy-2-phenyltetralone-1 even at room temperature on a two day standing with concentrated sulfuric acid. Attempts to cyclize the acid (I, R = p-CH₃O) under these conditions were found to be unsuccessful; only traces of the tricyclic methoxyketone were formed in this case.

In order to convert the acid (I, R = p-CH₃O) into 3-keto-6-methoxyhexahydrophenanthrene, Krollpfeiffer and Schäfer's discovery [4] which showed that γ -(p-anisyl)butyric acid chloride readily cyclized upon vacuum distillation with the cleavage of hydrogen chloride, was applied.

2-(γ -Chloro)crotyl-7-methoxytetralone-1 (IX) was formed in 80% yield by the distillation of the acid chloride (I, R=p-CH₃O) prepared by the reaction of the acid with phosphorus pentachloride. The latter was an o,o'-substituted tetralone and did not form a semi-carbazone even upon prolonged standing with semicarbazide solution.

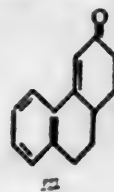
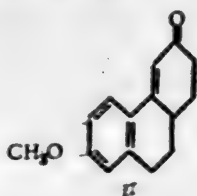
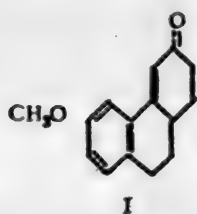


It could have been assumed that ketone (IX), like other γ, δ -unsaturated δ -chloroketones [10] would be subjected to hydrolysis by sulfuric acid followed by cyclization under mild conditions which would practically exclude the possibility of excessive sulfonation. Actually, 3-keto-6-methoxyhexahydrophenanthrene (II, R=6-CH₃O) was formed in a yield of 63.5% by the action of cold sulfuric acid (d 1.74) on ketone (IX).



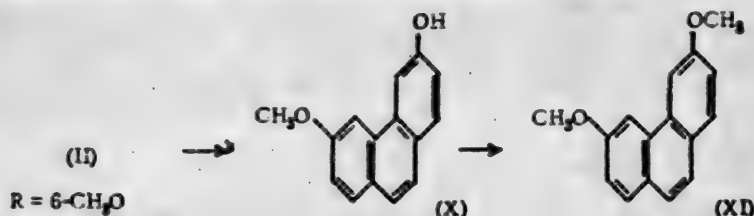
The absorption spectra of the methoxy ketones synthesized, as well as that of the unsubstituted 3-ketohexahydrophenanthrene obtained previously [1.11] were obtained by the method of photographic spectrophotometry. The dimming of the light rays was accomplished by rotating the sector with varying angles of exposure. The spectrograms were photometerized on the MF-2 microphotometer. Ethyl alcohol, carefully purified and optically transparent in the region investigated, served as the solvent.

The ultraviolet absorption curves of three investigated ketones (Fig. 1) are similar in their form and position of the maximum to those of benzalacetone and compounds having the system of conjugated double bonds of the latter in their molecules [12]. The absorption curve of the 7-methoxy derivative, in comparison to those of the other two ketones, is shifted strongly toward the longer wave lengths; its maximum differs from that of the other two curves by 35-40 mμ. This phenomenon can be explained by the presence of the para methoxyl group, which causes a shift of the electron density in the direction of the carbonyl group from the methoxyl leading to an increase in length or effective configuration of the system of double bonds.



On the curve of the 6-methoxy derivative, in whose molecule the possibility of such a shift is excluded by the presence of a meta methoxyl group, the maximum coincides with that of the unsubstituted 3-ketohexahydrophenanthrene. However, there is a small bulge on the lower part of this curve. Since this bulge coincides in wavelength with the maximum in the curve of the 7-methoxy derivative (320-325 m μ), the above circumstance can be explained by the presence of the 7-methoxy derivative as an impurity in the investigated 3-keto-6-methoxyhexahydrophenanthrene preparation. The presence of this impurity may be explained by the formation of a small amount of m-bromoanisole during the bromination of the starting material, anisole, to give p-bromoanisole.

In view of the fact that 3-keto-6-methoxyhexahydrophenanthrene was prepared by a method somewhat different from that used for the synthesis of the other ketones of this series, and because the 7-methoxy isomer was assumed to be present in the investigated preparation of this substance, it was subjected to dehydrogenation with sulfur in order to prove its structure and possibly establish the presence of the isomer. 3-Hydroxy-6-methoxyphenanthrene (X) was obtained which was then methylated to 3,6-dimethoxyphenanthrene (XI) [13].



The isomeric 2,6-dimethoxyphenanthrene [13], whose formation could have been expected with the presence of the 7-isomer in the starting methoxy ketone, could not be detected, which however, can not be regarded as proof of its complete absence.

EXPERIMENTAL

The starting β -(m-anisyl)ethylbromide was prepared from m-iodoanisole [14] by the action of ethylene oxide on its magnesium derivative, followed by reaction of the β -(m-anisyl)ethyl alcohol with phosphorus tribromide [3b]. β -(p-Anisyl)ethyl bromide [15] was obtained by the same method from p-bromoanisole.

β -(m-Anisyl)ethylmalonic ester (III. m-CH₃O)

98 g of β -(m-anisyl)ethyl bromide was added gradually to the sodium derivative of malonic ester prepared in 150 ml of absolute alcohol from 11.5 g of sodium and 80 g of malonic ester. The mixture was boiled on the water bath for 4 hours, a large part of the alcohol was distilled off, water acidified with hydrochloric acid was added to the residue, the product was extracted with ether, the ether solution was washed with water, and dried with anhydrous sodium sulfate. After the removal of the ether, the residue was twice vacuum distilled. 67 g (50% of the theoretical amount) of an almost colorless oil with b.p. 175-180° at 3 mm; d_4^{20} 1.1146; n_D^{20} 1.4960. Found M_{RD} 77.05. $C_{16}H_{21}O_5$. Calculated 77.43.

0.1058 g substance: 0.2547 g CO₂; 0.0762 g H₂O. 0.1044 g substance: 0.2496 g CO₂; 0.0712 g H₂O.
 Found %: C 65.65, 65.20, H 8.00, 7.57. $C_{16}H_{21}O_5$. Calculated %: C 65.31; H 7.48.

β -(p-Anisyl)ethylmalonic ester (III. p-CH₃O)

230 g (78.23% of the theoretical amount) of the previously [16] reported ester was obtained in an analogous manner from 180 g of malonic ester, 23 g of sodium, and 215 g of β -(p-anisyl)ethylbromide in 380 ml of absolute alcohol. The preparation obtained had the following properties: b.p. 174-176° at 2 mm; d_4^{20} 1.1003; n_D^{20} 1.4999, M_{RD} 78.62; calculated 77.43.

β -(m-Anisyl)ethyl(γ -chloro)crotyl malonic ester (IV. m-CH₃O)

60 g of β -(m-anisyl)ethylmalonic ester was added to a solution of sodium alcoholate prepared from 4.7 g of sodium in 64 ml of absolute alcohol. The mixture was heated for a half hour on the water bath. Upon cooling, 27.5 g of freshly redistilled 1,3-dichlorobutene-2 was added dropwise with stirring. The mixture was boiled for 4 hours and half of the alcohol used initially was distilled off; the residue in the flask was cooled and diluted with acidified water until complete solution of the precipitated salts; the reaction product was dissolved in ether, the ether solution was washed with water, and dried with anhydrous sodium sulfate. After the removal of the ether, the

residue was vacuum distilled. 67.5 g (86.5% of the theoretical amount) of a light-yellow thick oil boiling at 205-209° at 3 mm was obtained: d_4^{25} 1.1246; n_D^{25} 1.5087, Found MR_D 101.50. $C_{23}H_{27}O_3Cl$. Calculated 100.31.

0.1009 g substance: 0.0374 g AgCl. 0.1034 g substance: 0.393 g AgCl. Found %: Cl 9.17, 9.40. $C_{23}H_{27}O_3Cl$. Calculated %: Cl 9.28.

[8-(p-Anisyl)ethyl-(γ-chloro)crotyl] malonic ester (IV. p-CH₃O)

328 g (85% of the theoretical amount) of an almost colorless thick liquid with b.p. 221-223° at 6 mm was obtained by the above-reported method from 23 g of sodium, 312 ml of absolute alcohol, 294 g of 8-(p-anisyl) ethylmalonic ester, and 135 g of dichlorobutene: d_4^{25} 1.1349; n_D^{25} 1.5123. Found MR_D 101.11. $C_{23}H_{27}O_3Cl$. Calculated 100.31.

0.1094 g substance: 0.0412 g AgCl. 0.1140 g substance: 0.0430 g AgCl. Found %: Cl 9.34, 9.34. $C_{23}H_{27}O_3Cl$. Calculated %: Cl 9.28.

[8-(m-Anisyl)ethyl-(γ-chloro)crotyl] malonic acid (V. m-CH₃O)

A mixture of 68.3 g of the disubstituted malonic ester (IV. m-CH₃O), 22.7 g of sodium hydroxide, and 320 ml of 90% alcohol was refluxed for 5 hours with 200 ml of water, and the alcohol distilled off completely. The cooled aqueous solution was acidified, the precipitated product dissolved in ether, the ether solution washed with water, and dried with sodium sulfate. After the removal of the ether, 52 g (89.2% of the theoretical amount) of light yellow crystals was obtained. Recrystallized from a mixture of benzene and alcohol, colorless crystals with m.p. 138-139° were obtained.

0.1002 g substance: 0.0450 g AgCl. 0.1004 g substance: 0.0468 g AgCl. Found %: Cl 11.11, 11.06. $C_{18}H_{19}O_3Cl$. Calculated %: Cl 10.87.

[8-(p-Anisyl)ethyl-(γ-chloro)crotyl] malonic acid (V. p-CH₃O)

99.5 g (77.73% of the theoretical amount) of the impure light yellow crystalline product was obtained by the saponification of 150 g of the disubstituted malonic ester (IV. p-CH₃O) by a solution of 50 g of sodium hydroxide in 700 ml of 90% alcohol. After recrystallization from hot water, the acid was obtained in the form of colorless crystals with m.p. 136-137°.

0.1102 g substance: 0.0498 g AgCl. 0.1066 g substance: 0.0480 g AgCl. Found %: Cl 11.18, 11.14. $C_{18}H_{19}O_3Cl$. Calculated %: Cl 10.87.

α-(3-Chlorocrotyl)-γ-(m-anisyl)butyric acid (L. R = m-CH₃O)

50.3 g of the unrecrystallized dibasic acid (V. m-CH₃O) was decarboxylated by heating until the evolution of carbon dioxide ceased. The oil which formed was vacuum distilled. 40 g (91.9% of the theoretical amount) of a light-yellow, very viscous liquid with b.p. 207-210° at 5 mm was obtained: d_4^{25} 1.1514; n_D^{25} 1.5354. Found MR_D 76.44. $C_{15}H_{19}O_3Cl$. Calculated 75.44.

0.1056 g substance: 0.0536 g AgCl. 0.1041 g substance: 0.0536 g AgCl. Found %: Cl 12.56, 12.73. $C_{15}H_{19}O_3Cl$. Calculated %: Cl 12.56.

α-(3-Chlorocrotyl)-γ-(p-anisyl)butyric acid (L. R = p-CH₃O)

62.2 g (89.8% of the theoretical amount) of a viscous yellowish-green liquid, boiling at 192-193° at 3 mm was obtained by the decarboxylation of 80 g of the crude dibasic acid (V. p-CH₃O): d_4^{25} 1.1595; n_D^{25} 1.5396. Found MR_D 76.39. $C_{15}H_{19}O_3Cl$. Calculated 75.44.

0.1098 g substance: 0.0550 g AgCl. 0.1078 g substance: 0.0548 g AgCl. Found %: Cl 12.40, 12.58. $C_{15}H_{19}O_3Cl$. Calculated %: Cl 12.56.

3-Keto-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II. R = 7-CH₃O)

a) 30 ml of sulfuric acid (d 1.78) was added gradually with stirring and cooling with ice water to 5 g of the substituted butyric acid. The cherry-red solution was left to stand at room temperature for a half hour until foaming caused by the voluminous evolution of hydrogen chloride ceased, and then was heated for 3 hours at 60-65° on the water bath in a stream of carbon dioxide, and left to stand over night. On the following day, the reaction mixture was poured on ice, the precipitated oil-like substance was dissolved in ether, the ether solution washed thoroughly

with dilute alkali, then with water, and dried with sodium sulfate. Upon the acidification of the alkaline wash solution, it clouded slightly but the formation of an insoluble substance did not occur. After the removal of the ether, 2.9 g of a yellowish crystalline substance remained, which was recrystallized from alcohol (boiling with carbon). 2.3 g (57% of the theoretical amount) of colorless crystals with m.p. 114-115° was obtained.

0.1018 g substance: 0.2948 g CO₂; 0.0682 g H₂O. 0.1004 g substance: 0.2899 g CO₂; 0.0650 g H₂O.
0.2179 g substance: 0.2305 g AgI. Found %: C 78.96, 78.74; H 7.18, 7.19; CH₃O-group 13.50.
C₁₄H₁₂O(COCH₃). Calculated %: C 78.94; H 7.02; CH₃O-group 13.59.

The 2,4-dinitrophenylhydrazone, obtained by heating 0.3 g of the ketone and 0.26 g of dinitrophenylhydrazine in 40 ml of alcohol, formed dark-red light needles with m.p. 219-220° after recrystallization from a mixture of chloroform and alcohol.

0.1010 g substance: 13.5 ml N₂ (23°, 678 mm). Found %: N 13.75. C₂₁H₁₃O₅N₄. Calculated %: N 13.72.

b) 5 g of the acid (L R = m-CH₃O) was treated with 30 ml of sulfuric acid (d 1.78) under conditions analogous to those of the previous experiment, with the only difference being that, during the heating of the reaction mixture, the bath temperature was kept within the limits of 30-60°, and the mixture was processed directly after the 3 hour heating. 2.7 g of yellowish oily crystals was obtained, colorless, with m. p. 56-60° after recrystallization from alcohol.

0.1012 g substance: 0.2796 g CO₂; 0.0712 g H₂O. Found %: C 75.35; H 7.81.

The product, a mixture of the ketomethoxyhexahydrophenanthrene with the intermediate bicyclic diketone, was boiled for 2 hours with 20 ml of a 20% sodium hydroxide solution and then twice recrystallized from alcohol (boiling with carbon). The colorless crystalline substance obtained had a m.p. 114-115° (3-keto-7-methoxyhexahydrophenanthrene).

Action of sulfuric acid on α-(3-chlorocrotyl)-γ-(p-anisyl) butyric acid.

15 g of the acid (L R = p-CH₃O) was treated with 80 ml of sulfuric acid (d 1.74) under the above-reported conditions (see experiment a). Upon mixing the sulfuric solution with ice water, a very small amount of a solid substance formed. The substance was dissolved in ether, the ether solution was washed with dilute alkali, then with water, and dried with sodium sulfate. The light yellow crystals remaining after the removal of the ether melted at 110-111° after recrystallization from alcohol (boiling with carbon). A mixed sample with 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (see below) melted at the same temperature.

A two weeks' standing at room temperature of a mixture of 10 g of the acid (L R = p-CH₃O) and 50 ml of sulfuric acid (d 1.94) also led to the formation of water-soluble sulfonic acids; only traces of the tricyclic methoxyketone were obtained.

2-(γ-Chloro)crotyl-7-methoxytetralone-1 (IX)

134 g of phosphorus pentachloride was added in small portions with stirring to a solution of 184 g of the acid (L R = p-CH₃O) in 300 ml of dry benzene in a distillation flask. At the end of the violent reaction, the mixture was heated on the water bath for a half hour; part of the benzene was distilled off during this heating. The water bath was removed and the remaining benzene, as well as the phosphorous oxychloride formed during the reaction, were distilled off at atmospheric pressure. The distillation of the residue in vacuum was accompanied by a voluminous evolution of hydrogen chloride. After redistillation of the substance, which was washed with alkali and water, and dried, 138.7 g (80.5% of the theoretical amount) of a light-yellow, thick oil with b.p. 181-183° at 4 mm was obtained; d_4^{25} 1.1761; n_D^{25} 1.5740.

0.1337 g substance: 0.0718 g AgCl. 0.1237 g substance: 0.0655 g AgCl. Found %: Cl 13.28, 13.30.
C₁₅H₁₇O₂Cl. Calculated %: Cl 13.42.

After a two months' standing with a solution of semicarbazide, the substance thickened considerably, but a crystalline semicarbazone could not be isolated from it.

3-Keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II. R = 6-CH₃O)

60 ml of sulfuric acid (d 1.74) was added in small portions with ice cooling to 45 g of ketone (IX). The mixture was left to stand overnight at room temperature. After 24 hours, the dark green solution was poured on ice, the precipitated product was rubbed with a glass rod and crystallized completely. The substance was filtered, washed with alkali and water, and dried. After recrystallization from alcohol (boiling with carbon), colorless

prisms with m.p. 111-112° were obtained. Yield, 24.7 g (63.67% of the theoretical amount).

0.1097 g substance: 0.3176 g CO₂; 0.0702 g H₂O. 0.1108 g substance: 0.3194 g CO₂; 0.0718 g H₂O.
0.2179 g substance: 0.2223 g AgI. 0.2094 g substance: 0.2155 g AgI. Found %: C 78.95, 78.61;
H 7.11, 7.27. CH₃O-group 13.44, 13.60. C₁₄H₁₂O(OCH₃). Calculated %: C 78.94; H 7.02; CH₃O-group
13.59.

The 2,4-dinitrophenylhydrazone, cinnabar colored, recrystallized from a mixture of chloroform and alcohol had a m.p. 233-234°.

0.1008 g substance: 19.6 ml N₂ (21°, 676 mm). Found %: N 13.95. C₂₁H₁₅O₃N₃. Calculated %: N 13.72.

3-Hydroxy-6-methoxyphenanthrene (X)

A mixture of 3 g of the ketone (II. R = 6-CH₃O) and 0.9 g sulfur was heated at 185-195° for $\frac{1}{2}$ hour until the evolution of hydrogen sulfide stopped. The viscous product which formed, dissolved almost completely upon rubbing with an excess amount of warm 10% sodium hydroxide solution. The solution was filtered from the small amount of the insoluble oily residue. Upon the acidification of the filtrate, the acidic dehydrogenation product separated in the form of an emulsion which soon formed flocculant crystals. After three recrystallizations from alcohol (boiling with carbon), 1.5 g (50.9% of the theoretical amount) of colorless thin crystals with m.p. 125° was obtained.

0.1018 g substance: 0.3012 g CO₂; 0.0526 g H₂O. 0.1014 g substance: 0.2994 g CO₂; 0.0520 g H₂O.
Found %: C 80.69, 80.52; H 5.73, 5.69. C₁₅H₁₂O₂. Calculated %: C 80.36; H 5.35.

The red picrate, recrystallized from alcohol, melted at 165-166°.

0.1007 g substance: 9.2 ml N₂ (29°, 676 mm). 0.1007 g substance: 9.5 ml N₂ (29°, 674 mm). Found %:
N 9.20, 9.47. C₂₁H₁₅O₃N₃. Calculated %: N 9.27.

3,6-Dimethoxyphenanthrene (XI)

1 g of dimethyl sulfate was added dropwise with stirring to a solution of 0.7 g of 3-hydroxy-6-methoxyphenanthrene in 25 ml of a 2% sodium hydroxide solution heated on the water bath. The mixture was heated for 15 minutes, 20 ml of a 4% sodium hydroxide solution added, and the heating continued for 15 minutes more. After cooling, the oily product was dissolved in ether, the ether solution washed with water, and dried with sodium sulfate. Upon the removal of the ether, needle-like crystals which melted at 104-105° after recrystallization from alcohol were obtained (3,6-dimethoxyphenanthrene [13]).

SUMMARY

1. α -(3-Chlorocrotyl)- γ -phenylbutyric acids containing a methoxyl group in the meta and para position of the aromatic ring were synthesized, and the products of the reaction of these acids with sulfuric acid were investigated.
2. It was shown for the example of α -(3-chlorocrotyl)- γ -(m-anisyl)butyric acid that the meta methoxyl group did not prevent the intramolecular acylation from occurring in the para position in relation to this group. The yield of the cyclization product was somewhat lower than those found for unsubstituted α -(3-chlorocrotyl)- γ -phenylbutyric acid and its aromatic methyl homologs, which, evidently, is explained by the favorable effect of the methoxyl group on the sulfonation of the starting acid.
3. Only traces of 3-keto-6-methoxyhexahydrophenanthrene, the product of the sulfuric acid hydrolysis and double cyclization of the latter, were formed by the action of sulfuric acid on α -(3-chlorocrotyl)- γ -(p-anisyl)butyric acid, which is explained by the effect of the para methoxyl group favoring the sulfonation of the starting acid and hindering the intramolecular acylation occurring in the meta position relative to this group. A satisfactory yield of 3-keto-6-methoxyhexahydrophenanthrene could only be achieved by a different method based on the separate cyclization of rings B and C.

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INVESTIGATIONS OF ALKANE SULFONIC ACIDS

IX. SYNTHESIS AND PROPERTIES OF ARYLAMIDES OF PHENYLMETHANESULFONIC ACIDS

A. G. Kostsova

A series of arylamides of phenylmethanesulfonic acid are reported in the present communication. The arylamides of methane and chloromethanesulfonic acids were reported in detail in the previous communications [1]. Reactions of phenylmethanesulfonyl chloride with aniline, o,p-toluidine, p-anisidine, p-phenetidine, and α -aminopyridine were conducted. It was found that phenylmethanesulfonyl chloride showed a sufficiently great reactivity: it reacts with the above amines under various conditions although somewhat more slowly than the alkanesulfonyl chlorides, which possess very high reactivity.

The anilide, o,p-toluidide, p-anisidide, p-phenetidide, and α -aminopyridide obtained are colorless, crystalline substances readily soluble in ether, alcohol, benzene, difficultly in water, dissolve in alkalis, and separate from the alkaline solutions upon acidification; they are sufficiently stable to hydrolysis, i.e., they show a great resemblance in properties to the aryl amides of alkane sulfonic acids.

The general equation for the reaction is the following:



EXPERIMENTAL

The following of the series of experiments conducted are given below: the starting phenylmethanesulfonyl chloride was prepared by the chlorination of phenylmethyl thiocyanate. An energetic stream of chlorine was passed for 1.5 hours at room temperature (18-20°) into a suspension of 4 g of freshly prepared phenylmethyl thiocyanate (m.p. 41°) in 30 ml of water. The temperature of the mixture rose to 50° and once more fell to 20-25°. The sulfonyl chloride accumulated on the bottom of the reaction vessel in the form of a dense yellow oil. At the end of the reaction, the mixture was cooled. The oily sulfonyl chloride gradually crystallized. The residue was filtered, washed several times with water, 5% sodium carbonate solution, once more with water, and then dried. Yield 1.25 g or 25% of the theoretical. A more prolonged chlorination at lower temperatures led to an insignificant yield of the sulfonyl chloride. Phenylmethanesulfonyl chloride, white crystals with m.p. 94°, was soluble in ether, benzene, acetone, and insoluble in water; it has an irritating action on skin.

1. Reaction of phenylmethanesulfonyl chloride with aniline. The procedure for conducting the reaction of phenylmethanesulfonyl chloride with aniline, as well as the isolation and purification of the reaction product, is reported in great detail; all of the subsequent experiments were conducted in an analogous manner; for this reason reports of subsequent experiments are omitted. 1.5 g of phenylmethanesulfonyl chloride was dissolved in 30 ml of absolute ether. 1.47 g of aniline was added to the solution in small portions. The solution clouded, and after 30-40 minutes aniline hydrochloride precipitated. The salt was filtered after 3-4 hours and was not investigated further. The ethereal filtrate was evaporated. The residue was treated with dilute alkali, the impurities insoluble in alkali were filtered, and the reaction product, phenylmethanesulfonilide, was precipitated with dilute sulfuric acid. It was recrystallized from alcohol and water; m.p. 109°. Yield 0.63 g or 35% of the theoretical. A reaction in ether with heating on the water bath at 50° with reflux led to the same results. A reaction in absolute benzene with heating at 90° gave a yield of 70% of the theoretical of the product.

0.0389 g substance: 1.58 ml 0.1 N H_2SO_4 . 0.1508 g substance: 0.1408 g BaSO_4 . Found %: N 5.69; S 12.82. $\text{C}_{13}\text{H}_{13}\text{O}_3\text{NS}$. Calculated %: N 5.66; S 12.95.

2. Reaction of phenylmethanesulfonyl chloride with o-toluidine. 2 g of the chloride, 80 ml of absolute ether, and 2.2 g of o-toluidine were used. By dissolving the crude reaction product in alkali and by subsequently precipitating it with acid, it was isolated in the form of a yellow oil which crystallized only upon strong

• N. P. Venevitinova and M. A. Gorshkova participated in the experimental work.

cooling. The crystals were greasy to touch. M.p. 65°. Yield 2.1 g or 78% of the theoretical. The reaction in absolute ether at room temperature lowered the yield to 55-56%; in benzene with heating the yield was 74-85%, at room temperature, 48-49% of the theoretical.

0.1018 g substance: 3.84 ml 0.1 N H_2SO_4 . 0.1012 g substance: 0.0905 g BaSO_4 . Found %: N 5.28; S 12.20. $\text{C}_{14}\text{H}_{15}\text{O}_2\text{NS}$. Calculated %: N 5.34; S 12.26.

3. Reaction of phenylmethanesulfonyl chloride with *p*-toluidine. The reaction was conducted with the same quantities of starting materials as in the previous experiment. Phenylmethanesulfo-*p*-toluidide was a white finely crystalline substance. M.p. 108°. Yield 1.5 g or 69-70% of the theoretical. The reaction in ether at room temperature gave a yield of 46% of the product, in benzene upon heating, 60%, at room temperature, 41-42% of the theoretical.

0.1020 g substance: 3.85 ml 0.1 N H_2SO_4 . 0.1015 g substance: 0.0911 g BaSO_4 . Found %: N 5.28; S 12.30. $\text{C}_{14}\text{H}_{15}\text{O}_2\text{NS}$. Calculated %: N 5.34; S 12.26.

4. Reaction of phenylmethanesulfonyl chloride with *p*-anisidine. 1.7 g of phenylmethanesulfonyl chloride, 2.1 g of *p*-anisidine, and 50 ml of absolute ether were used. Phenylmethanesulfo-*p*-anisidine was a white crystalline substance bitter to the taste. M.p. 101°. The yield was 1.1 g or 46% of the theoretical. The reaction in ether without heating gave a yield of 43%, in benzene upon heating 64-65% of the theoretical.

0.0380 g substance: 1.469 ml 0.1 N H_2SO_4 . 0.1037 g substance: 0.0889 g BaSO_4 . Found %: N 5.40; S 11.75. $\text{C}_{14}\text{H}_{15}\text{O}_2\text{NS}$. Calculated %: N 5.05; S 11.55.

5. Reaction of phenylmethanesulfonyl chloride with *p*-phenetidine. 2 g of phenylmethanesulfonyl chloride, 2.8 g of *p*-phenetidine, and 90 ml of absolute ether were used. Phenylmethanesulfo-*p*-phenetidine was obtained in the form of needles; m.p. 110°. Yield 1.9 g or 87% of the theoretical. The reaction in ether without heating gave a yield of 55.6%, in benzene with heating 93%; without heating 87% of the theoretical.

0.1022 g substance: 3.47 ml 0.1 N H_2SO_4 . 0.0904 g substance: 0.0720 g BaSO_4 . Found %: N 4.75; S 10.92. $\text{C}_{15}\text{H}_{17}\text{O}_2\text{NS}$. Calculated %: N 4.79; S 10.99.

6. Reaction of phenylmethanesulfonyl chloride with α -aminopyridine. 2 g of phenylmethanesulfonyl chloride and 1.85 g of α -aminopyridine were dissolved in 20 ml of benzene. The mixture was shaken for 20-30 minutes. A clouding and a slight amount of heating occurred (23-25°). Soon a yellow oil formed on the bottom of the reaction flask. After standing for some time, the oil was separated and vacuum distilled; a small amount of unreacted α -aminopyridine was removed; the remaining part of the oil decomposed upon distillation. The benzene solution, after the removal of the oil, was evaporated in a porcelain dish. With the evaporation, light yellow scaly crystals of phenylmethanesulfo- α -aminopyridide precipitated on the walls of the dish. They became colorless upon recrystallization from water. Yield, 68% of the theoretical. M.p. 143°. Upon treatment with 5% alkali followed by acidification with sulfuric acid, the product precipitated only when there was a strictly neutral reaction; with an excess of acid, it dissolved, forming apparently, a water-soluble salt because of the tertiary nitrogen atom of the pyridine residue. Upon conducting the reaction in acetone at room temperature, the yield of the product was 1.97 g or 75-76% of the theoretical; in benzene and in acetone with heating, the crystalline product was not formed at all, or an oil separated from which definite compounds could not be isolated.

0.2331 g substance: 17.967 ml 0.1 N H_2SO_4 . 0.1836 g substance: 0.1690 g BaSO_4 . Found %: N 10.79; S 12.62. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_2\text{S}$. Calculated %: N 11.29; S 12.90.

SUMMARY

1. The reactions of phenylmethanesulfonyl chloride with aniline, *o*- and *p*-toluidine, *p*-anisidine, *p*-phenetidine, α -aminopyridine were studied under various conditions.

2. The anilide, *o*- and *p*-toluidide, *p*-anisidide, *p*-phenetidide, and α -aminopyridide of phenylmethanesulfonic acid were prepared and characterized for the first time.

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Received October 13, 1952

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INVESTIGATIONS OF IMIDAZOLE DERIVATIVES

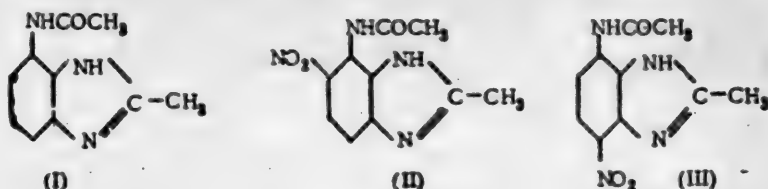
VIII. STUDY OF NITRATION AND AZOCOUPLING REACTIONS OF 4-AMINO BENZIMIDAZOLE [1]

L. S. Efros

The aim of the present investigation was to study the effect of amino group in position 4 of benzimidazole on the benzene ring of these compounds during nitration and azo coupling reactions.

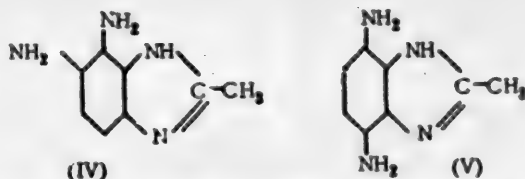
The start of the investigation was a study of the nitration of 4-acetylamino-2-methylbenzimidazole (I), which proceeded very smoothly in concentrated sulfuric acid.

The reaction product could be separated by means of crystallization from alcohol into two isomeric substances (II and III) which were obtained in an approximately 1:2 ratio.



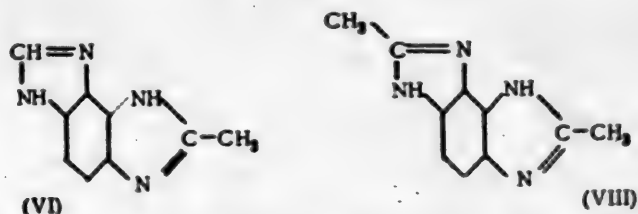
Both of these substances hydrolyzed readily upon boiling in dilute hydrochloric acid to form the free amines which were capable of diazotization, and subsequently, of participating in coupling reactions.

The amine from product (II), obtained in lower yield, was in the form of yellow platelets, the amine isomeric with it from product (III), light yellow needles. In order to prove the structure both amines were reduced with tin and hydrochloric acid into the unstable diamines (IV) and (V).



o-Diamine (IV) without further purification, was treated with anhydrous formic acid; another imidazole ring formed and a stable unhydrolyzable methyl derivative of diimidazolo-1,2,3,4- benzene (VI) unhydrdized upon treatment with acids, crystallizing from water in the form of white needles was obtained.

Analogously, upon treating diamine (IV) with glacial acetic acid in a sealed tube at 180°, dimethyldiimidazolo-1,2,3,4-benzene (VII) was obtained.

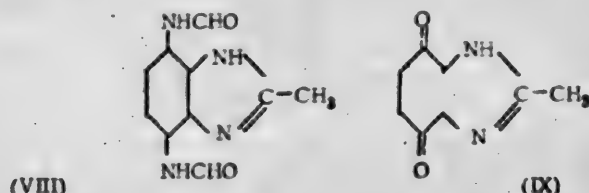


This compound (VII) was previously reported by Nietzki [2] who obtained it during the process of proving the structure of dinitrosoresorcinol.

However, according to Nietzki's data, the melting point of compound (VII) was lower than that for the product obtained by more than 100°. In view of this, the reported synthesis was repeated, and a substance was obtained in a very low yield which melted as the above and gave no depression upon mixing after thorough purification.

As for the *p*-diamine (V), it gave a stable and poorly-soluble salt with sulfuric acid, in which form it was possible to purify and analyze it. In contrast to diamine (IV), this compound only formed the diformyl derivative (VIII) upon boiling with formic acid, which was readily cleaved upon heating with mineral acids to form the unstable diamine.

By careful oxidation of the *p*-diamine (V) with chromic acid, a new interesting derivative of benzoquinone with an imidazole ring (IX) was obtained.

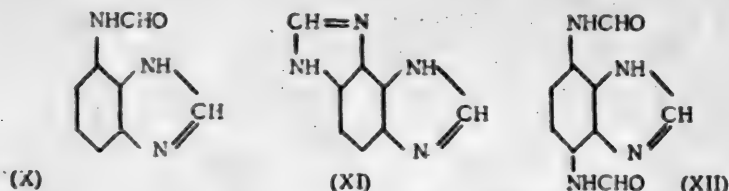


This compound, crystallizing in the form of bright orange-yellow needles, was found to be quite unstable. It dissolved readily in mineral acids with a light yellow color. In alkali solution, however, this compound decomposed very rapidly; the bright color of the solution almost at once became cloudy, and the starting substance could not be isolated from it. A noticeable decomposition of the product occurred even upon heating with water.

The nitration of 4-formaminobenzimidazole (X) was studied analogously.

In this case, the mixture of *ortho* and *para* aminonitro-derivatives could not be successfully separated, which was obtained by nitration; for this reason, the mixture of these substances, after treatment with hydrochloric acid, was reduced with tin, and without any further purification, treated with anhydrous formic acid. The reaction product was separated into two substances by recrystallization from water; one of these, obtained in smaller amount, was found to be stable to hydrochloric acid treatment, and had the structure of diimidazo-1,2,3,4-benzene (XI).

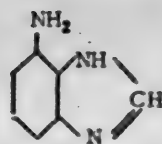
The other product, readily hydrolyzable by boiling with hydrochloric acid, is the diformyl derivative of *p*-diamine (XII).



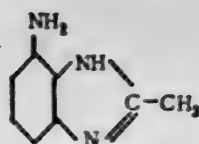
Upon treatment of the reduction products of this mixture of nitro compounds with acetic acid in a sealed tube at 180°, methyl-diimidazo-1,2,3,4-benzene was isolated which was found to be identical with the previously reported compound (VI) obtained by the condensation of *o*-diamine (IV) with formic acid. In this way, it was proved that, during nitration of acyl derivatives of 4-aminobenzimidazole, and 4-amino-2-methylbenzimidazole, a mixture of the *ortho* and *para* isomers of the corresponding aminonitro derivatives was obtained. More of the *para* isomer is contained in this mixture than the *ortho* isomer.

Later, the coupling reaction of 4-aminobenzimidazole (XIII) and 4-amino-2-methylbenzimidazole (XIV) with diazo compounds was studied.

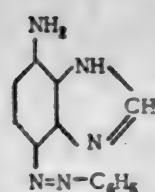
As expected, it was found that the substances readily participated in diazo coupling reactions. Dyes, obtained from them, upon coupling with diazotized aniline, (XV) and (XVI), were purified and analyzed.



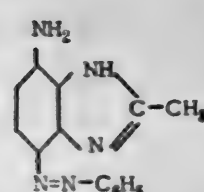
(XIII)



(XIV)



(XV)



(XVI)

The above structures for these substances were proved by reduction and subsequent treatment with anhydrous formic acid. The diformyl derivatives of 4,7-diaminobenzimidazole obtained were found to be identical with the previously reported compounds (VIII) and (XII) synthesized from 4,7-diaminonitrobenzimidazoles.

Therefore, the amino group found in position 4 of benzimidazole, has a large activating effect on the benzene ring of these compounds and made the coupling reaction with diazo compounds possible. The latter reaction goes exclusively para to the amino group (position 7), whereas during nitration, although in smaller yield, the ortho isomer is also obtained. The specific activity of positions 5 and 6 of benzimidazole is not affected.

EXPERIMENTAL

1. Nitration of Acyl Derivatives of 4-Aminobenzimidazole •

1. Nitration of 4-Acetylamino-2-methylbenzimidazole.

9 g of the product was dissolved in 60 ml of conc. sulfuric acid, keeping the temperature below 15-20°. Then, a nitrating mixture of 4 ml nitric acid (d 1.5) and 8 ml of conc. sulfuric acid was added dropwise at this temperature with stirring without allowing an increase in temperature. 15 minutes after the addition, the mass was poured onto ice, and the solution was carefully neutralized with ammonia with the addition of ice (temperature not higher than 40-50°). The light yellow product which separated was filtered, washed with water until not acid, and dried. The product obtained was dissolved with heating in alcohol and the hot solution was separated from a small amount of alcohol-insoluble impurities. Upon cooling, 7-nitro-4-acetylamino-2-methylbenzimidazole crystallized from it in the form of light yellow shiny platelets. A small amount more of this product was isolated upon the evaporation of the alcoholic mother liquor to one third the volume. The total yield of this isomer was 3.2-3.8 g.

The residue remaining after complete removal of the alcohol from the mother liquor, was mainly the second isomer, 5-nitro-4-acetylamino-2-methylbenzimidazole, partly saponified. It was very soluble in alcohol and did not crystallize from it. This residue was heated for 15-20 minutes with 5-10 ml of 10% hydrochloric acid. After cooling, the amine hydrochloride slowly separated in the form of orange-yellow square or rhombic platelets. The yield of this product was 1.3-1.6 g.

The acetyl derivative of 7-nitro-4-amino-2-methylbenzimidazole was a light-yellow, shiny, platelet-like crystalline substance with m.p. 315-318° (with preliminary softening and darkening).

0.1320 g substance: 0.2477 g CO₂; 0.0495 g H₂O. 0.1040 and 0.1065 g substance: 21.7, 23.3 ml N₂ (22°, 754 mm). Found %: C 51.20; H 4.17; N 23.95, 24.05. C₁₀H₁₀O₃N₄. Calculated %: C 51.30; H 4.27; N 23.90.

7-Nitro-4-amino-2-methylbenzimidazole. For saponification, 0.5 g of the product was dissolved in 15 ml of 5% hydrochloric acid; the hydrochloride precipitated and was dissolved upon heating. Soon however, long, light-yellow needles of 7-nitro-4-amino-2-methylbenzimidazole precipitated from the boiling solution. They were filtered and recrystallized from water containing hydrochloric acid.

0.1050 g substance. 0.0659 g AgCl. 0.1002 and 0.1005 g substance: 21.1 ml and 21.2 ml N₂ (22°, 762 mm).

Found %: N 24.5, 24.6; Cl 15.5. C₉H₈O₃N₄·HCl. Calculated %: N 24.5; Cl 15.5.

In order to convert to the base, the 7-nitro-4-amino-2-methylbenzimidazole salt was dissolved in water, carefully neutralized with ammonia, and recrystallized from water. Fine, light-yellow, shiny crystals with m.p. 291-293°.

0.1081 and 0.1098 g substance: 27.5 ml and 28.0 ml N₂ (22°, 760 mm). Found %: N 29.45, 29.5. C₉H₈O₃N₄. Calculated %: N 29.15.

• For the synthesis of 4-acetylamino-2-methylbenzimidazole, see the following communication (p. 93)

The reduction of the nitro group of this compound was effected in the following manner: 2 g of the hydrochloride was treated with heating with 5 g of granulated tin and 5 g of conc. hydrochloric acid. When the reaction was finished, the solution was poured from the residual tin, and the complex of the tin salt and the reduction product began to crystallize after some time. It was filtered, dissolved in water, the tin removed by passing a stream of hydrogen sulfide, and the filtrate evaporated in vacuum to dryness. A white crystalline compound was obtained which was very easily oxidized. It was dissolved in a small amount of water, and dilute sulfuric acid was added. A white needle like precipitate of the diamine sulfate formed which was purified by recrystallization from dilute hydrochloric acid using active carbon.

0.1173 and 1170 g substance: 0.1054 and 0.1050 g BaSO_4 . Found %: H_2SO_4 37.8, 37.65.
 $\text{C}_8\text{H}_{10}\text{N}_4 \cdot \text{H}_2\text{SO}_4$. Calculated %: H_2SO_4 37.70.

For the preparation of methylimidazobenzquinone, 2 g of the diamine hydrochloride (obtained directly by the reduction of the nitro product) was dissolved in 20 ml of water, a small amount of dilute sulfuric acid and a solution of 2 g of chromic acid in water was added. The amine sulfate which precipitated upon the addition of the sulfuric acid, dissolved quite rapidly; the solution was heated up to a slight extent by the oxidation reaction occurring. After a half hour, sodium acetate was added to the solution until the absence of an acidic reaction to Congo; the yellow needles of the quinone which precipitated were filtered, and washed with water. The product was purified by 3 times dissolving the product in cold dilute hydrochloric acid and precipitating with sodium acetate followed by washing with water. Yield 0.9 g. The product decomposed over 360° ; it did not melt.

The quinone was readily soluble in dilute mineral acids and alkalis with the formation of bright raspberry red solutions which, however, rapidly clouded because of the decomposition of the product. Upon heating with water, it also noticeably decomposed.

0.1409 and 0.1268 g substance: 0.3073 and 0.2770 g CO_2 ; 0.0493 and 0.0423 g H_2O . 0.1018 and 0.1030 g substance: 15 (18° , 762 mm) and 15.3 ml N_2 (20° , 758 mm).

Found %: C 59.40, 59.45; H 3.88, 3.71; N 17.30, 17.30. $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$. Calculated %: C 59.27; H 3.71; N 17.30.

In order to prepare the diformyl derivative of 4,7-diamino-2-methylbenzimidazole, 2 g of the diamine hydrochloride, obtained by the reduction of the nitro product, was dissolved by heating in 10 ml of anhydrous formic acid and refluxed for 2 hours. The solution was evaporated almost to dryness on the water bath, neutralized with ammonia and after cooling, the precipitated diformyl derivative of 4,7-diamino-2-methylbenzimidazole was filtered. Yield 1.2 g. The product was recrystallized from water over active carbon. White thin needles with m.p. $268-270^\circ$. (with initial softening). The compound obtained was readily hydrolyzed by hydrochloric acid with heating. The solution obtained in this manner, after neutralization with ammonia, darkened very rapidly, then turned black, and nothing could be isolated from it but dark tarry flocs. Upon conducting the reaction with sulfuric acid, needles of the diamine sulfate reported above came out of the solution.

0.1210 g substance: 0.2440 g CO_2 ; 0.0500 g H_2O . 0.1168 and 0.1003 g substance: 26.2 and 22.3 ml N_2 (22° , 753 mm). Found %: C 54.90; H 4.59; N 25.7; 25.5. $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2$. Calculated %: C 54.95; H 4.58; N 25.7.

5-Nitro-4-amino-2-methylbenzimidazole. The hydrochloride crystallized from aqueous hydrochloric acid as bright yellow square or rhombic platelets. It was considerably more soluble in water than the salt of the second isomer. It did not have a definite melting point.

0.0980 and 0.0951 g substance: 21 and 20.5 ml N_2 (22° , 754 mm). 0.0672 g substance: 0.0420 g AgCl . Found %: N 24.5, 24.7; Cl 15.4. $\text{C}_8\text{H}_8\text{O}_2\text{N}_4 \cdot \text{HCl}$. Calculated %: N 24.5; Cl 15.3.

The base of the product was obtained by treating the salt with an ammonia solution and recrystallization from aqueous alcohol. Yellow crystals with m.p. $300-302^\circ$.

0.0598 and 0.0734 g substance: 15.2 and 18.6 ml N_2 (22° , 760 mm). Found %: N 29.3, 29.3. $\text{C}_8\text{H}_8\text{O}_2\text{N}_4$. Calculated %: N 29.15.

The reduction of the product was effected, as in the previous case, with tin and hydrochloric acid. The yield from 2 g of the hydrochloride was 0.9-1.1 g of diamino-2-methylbenzimidazole hydrochloride. The product, without further purification, was dissolved in 10 ml of anhydrous formic acid and refluxed for 2 hours. The solution was evaporated almost to dryness on the water bath, dissolved in water, and the reaction product precipitated

with ammonia. Yield 0.8-0.9 g. Methyl-1,2,3,4-diaminodimidazobenzene obtained in this manner, was recrystallized from water; long white needles with m.p. 312-314°. It was readily soluble in dilute hydrochloric acid, it was not decomposed by prolonged boiling, and was precipitated from solution by the addition of ammonia:

0.0910 g substance: 0.2976 g CO₂; 0.0403 g H₂O. 0.1032 and 0.1035 g substance: 29.0 and 29.0 ml N₂ (22°, 762 mm). Found %: C 62.20; H 4.00; N 32.70, 32.65. C₈H₈N₄. Calculated %: C 62.80; H 4.65; N 32.55.

1 g of 4,5-diamino-2-methylbenzimidazole hydrochloride was heated in a sealed tube with 7 ml glacial acetic acid at 180° for 1 hour. The liquid was evaporated to dryness, the residue dissolved in water, and dimethyl-1,2,3,4-dimidazobenzene precipitated with ammonia. Yield 0.6 g. The product was purified by recrystallization from water; white needles with m.p. 292-294°. It was readily soluble in alcohol, poorly in water (about 1 g of the product dissolved in 100 ml of boiling water); it was readily soluble in dilute hydrochloric acid and unchanged upon continued heating with it.

0.1002 and 0.0991 g substance: 0.2350 and 0.2331 g CO₂; 0.0482 and 0.0479 g H₂O. 0.1161 and 0.1101 g substance: 30.4 (22°, 754 mm) and 28.7 ml N₂ (20°, 754 mm). Found %: C 63.96, 64.20; H 5.58, 5.37; N 30.1, 30.2. C₁₀H₁₀N₄. Calculated %: C 64.5; H 5.4; N 30.1.

2. Nitration of 4-Formaminobenzimidazole. 11 g of formaminobenzimidazole was carefully dissolved in 40 ml of conc. sulfuric acid, and a nitrating mixture of 3.5 ml of nitric acid (d 1.5) and 1.5 ml of sulfuric acid was added dropwise at 10-15° to the solution. The reaction mass was poured onto ice and carefully neutralized with ammonia, not allowing the solution to heat up. The yellow nitration product which separated was filtered and washed with water. Yield 9 g. The product, without further purification, was reduced by 15 g of tin and 20 ml of conc. hydrochloric acid. The complex which separated was dissolved after filtration, the tin precipitated with hydrogen sulfide, and the solution obtained evaporated to dryness in vacuum. The residue was boiled with 30 ml of anhydrous formic acid for 2 hours, the formic acid was evaporated, the residue dissolved in water, and the reaction product precipitated with ammonia. The reaction product was subjected to fractional crystallization from water. The more difficultly soluble 1,2,3,4-dimidazobenzene, obtained in a yield of 2.5-3.0 g, crystallized. 1,2,3,4-Dimidazobenzene was boiled with 5% HCl, precipitated from ammonia solution, and recrystallized from water with activated carbon for complete purification from the second product. Yield 0.5-0.9 g; m.p. 288-296°.

0.1055 g substance: 0.2360 g CO₂; 0.0361 g H₂O. 0.1032 g and 0.1036 g substance: 31.8 ml and 31.8 ml N₂ (21°, 754 mm). Found %: C 60.90; H 3.80; N 35.50, 35.50. C₈H₆N₄. Calculated %: C 60.75; H 3.80; N 35.45.

4,7-Diforaminobenzimidazole was a long, needle-like crystalline substance readily soluble in dilute hydrochloric acid. M.p. 292-293°.

0.1354 and 0.1215 g substance: 0.2602 and 0.2360 g CO₂; 0.0500 and 0.0478 g H₂O. 0.1120 and 0.1430 g substance: 27 (22°, 754 mm) and 34.4 ml N₂ (22°, 758 mm). Found %: C 52.30, 52.95; H 4.18, 3.93; N 27.70, 27.70. C₈H₆O₂N₄. Calculated %: C 52.90; H 3.92; N 27.45.

3 g of the above product of the reduction of the nitro compound was heated with 15 ml of glacial acetic acid at 180° in a sealed tube for 1 hour. The condensation product, precipitated by neutralization with ammonia, was treated with hydrochloric acid with heating to remove the acetyl derivative, precipitated with ammonia, and purified by recrystallization from water with active carbon. A yield of 0.3 g of methyl-1,2,3,4-dimidazobenzene was obtained, which was identical in properties with that previously obtained.

II. Coupling of 4-Aminobenzimidazole and Its 2-Methyl Derivative with Diazotized Aniline

8 g 4-aminobenzimidazole dihydrochloride was dissolved in 50 ml of water; diazotized aniline and sodium acetate were added to the solution until the absence of an acidic reaction on Congo. A coupling occurred which resulted in the solution turning orange, and upon standing, an azo dye began to precipitate. After an hour, it was filtered, washed with a small amount of water, pressed, and dried. Yield 12 g.

The dye, in the form of the monohydrochloride, crystallized from water in the form of red needles not having a definite melting point. Aqueous solutions were colored red-orange; upon the addition of hydrochloric acid, they became violet red; upon the addition of ammonia, the dye base precipitated in the form of a tar.

0.1023 and 0.1030 g substance: 23.0 and 23.1 ml N_2 (22°, 754 mm). 0.0922 and 0.0957 g substance. 0.0482 and 0.0503 g AgCl. Found %: N 25.80, 25.80; Cl 12.92, 13.02. $C_{13}H_{13}N_3 \cdot HCl$. Calculated %: N 25.70; Cl 13.03.

The coupling of diazotized aniline with 4-amino-2-methylbenzimidazole was effected in an analogous manner. 7 g of the dye, in the form of the monohydrochloride, was obtained from 6 g of the amine dihydrochloride. Its properties were similar to those of the one previously described.

0.1183 and 0.1119 g substance: 25.6 and 23.7 ml N_2 (22°, 754 mm). 0.1003 g substance: 0.0497 g AgCl. Found %: N 24.80, 24.35; Cl 12.50. $C_{14}H_{13}N_3 \cdot HCl$. Calculated %: N 24.45; Cl 12.37.

In order to prove the structures, both dyes were reduced with tin and hydrochloric acid. The complex which precipitated was dissolved in water, and the tin was removed with hydrogen sulfide. The filtrate was evaporated to dryness in vacuum, and the solid white residue of the amine salts obtained was boiled for 2 hours with anhydrous formic acid. The formic acid solution obtained was evaporated to dryness on the water bath, the residue was dissolved in water, and the reaction product, precipitated by the action of ammonia, was purified by recrystallization from water with activated carbon. Products were obtained which were found to be identical with the previously reported diformyl derivatives of 4,7-diaminobenzimidazole and 2-methyl-4,7-diaminobenzimidazole.

SUMMARY

The amino group found in position 4 of benzimidazole has a great activating effect on the benzene ring of these compounds. Because of this effect, 4-aminobenzimidazoles readily participate in azo coupling reactions to form p-amino azo dyes exclusively. Upon the nitration of acyl derivatives of 4-aminobenzimidazole, mixtures of ortho and para nitro derivatives containing a larger amount of the para isomer were obtained.

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Received July 1, 1952

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* See Consultants Bureau English Translation, p. 881.

** See Consultants Bureau English Translation, p. 1053

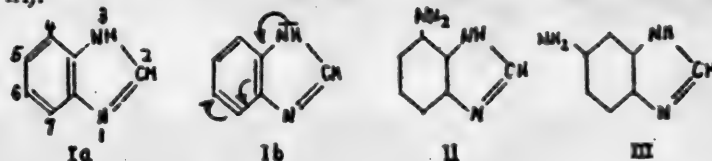
INVESTIGATIONS OF IMIDAZOLE DERIVATIVES

IX. SYNTHESIS OF 4-AMINOBENZIMIDAZOLE AND COMPARISON OF ITS CHEMICAL PROPERTIES WITH THOSE OF 5-AMINOBENZIMIDAZOLE [1]

L. S. Efros

In the previous investigations [2,3], it was shown that the imidazole group causes a considerable destruction of symmetry in relation to the benzene ring in the benzimidazole molecule wherein the double bond character of the 4-5 and 6-7 carbon atoms increases while the 5-6 carbon atom bond resembles the regular ones. With such a distribution of bonds, benzimidazole (Ia) must resemble naphthalene [4] in its chemical properties; however, in contrast to the latter, positions 5 and 6, not 4 and 7, possess greater reactivity in the compounds examined, which correspond to the less active position in naphthalene. The reason for the above behavior of benzimidazole is the direction of the effect of the nitrogen atoms of the heterocycle, which is transferred along a chain of conjugated double bonds. The reactive ends of these chains are found in positions 5 and 6 because there is a certain amount of disruption in conjugation between these positions (Ib).

From this point of view, it seemed interesting to compare the chemical properties of 4-amino- and 5-amino-benzimidazole (II and III):



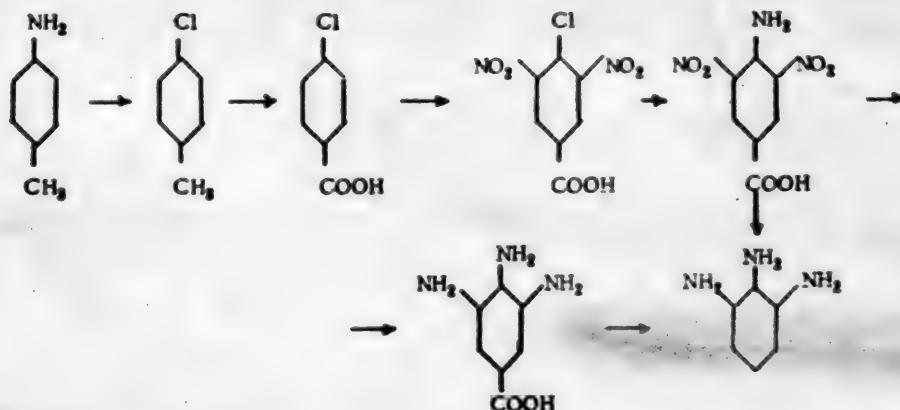
It would be expected that the amino group in the unreactive benzimidazole position 4 would not noticeably affect the basicity of the compound, while the effect of the amino group in position 5 must be considerable.

It seemed of interest to study the effect of the amino groups of these compounds on the benzene ring. This study could determine whether or not the above-mentioned interruption in the conjugation between carbon atoms 5 and 6 in the benzimidazole was retained with the presence of an amino group in position 4; if it was retained, then the substitution reactions with compounds of type II must occur preferentially at the o-position to the amino group (position 5); if it was not retained, at the p-position (position 7).

The preparation of 5-aminobenzimidazole derivatives did not entail any sort of difficulty. They were synthesized by the reduction of the corresponding nitro derivatives obtained by the nitration of the benzimidazoles.

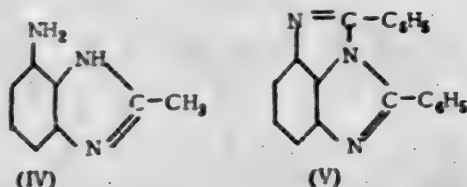
As for the 4-aminobenzimidazole derivatives, it was necessary to synthesize the ordinary triaminobenzene. The formation of the latter by the decarboxylation of 3,4,5-triaminobenzoic acid was reported by Salkowsky [5].

The synthesis of the ordinary triaminobenzene was accomplished by the following scheme:

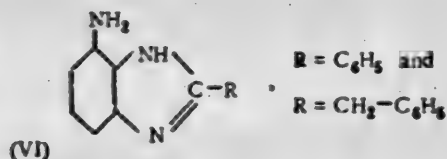


The overall yield of triamino benzene was 27.2 % of the theoretical. By heating the product with anhydrous formic acid, the formyl derivative of 4-aminobenzimidazole was obtained, from which the free amine (II) was formed by saponification with hydrochloric acid.*

By heating triaminobenzene with acetic acid and subsequent saponification, the previously reported by Salkowsky, 4-amino-2-methylbenzimidazole (IV) and its acetyl derivative were obtained.



Attempts to obtain analogous products by the fusion of ordinary triaminobenzene with benzoic acid and phenylacetic acid were unsuccessful. Substances were obtained in reactions under these conditions, which did not contain amino groups and did not cleave even upon prolonged boiling with hydrochloric acid. It is possible that these compounds were products of a further cyclization of the acylaminobenzimidazole of structure (V), which Auwers and Fresle [9] tried unsuccessfully to prepare. For this reason, the 4-amino-2-phenylbenzimidazoles and 4-amino-2-benzylbenzimidazoles which were of further interest and unreported in the literature, were obtained by the condensation of triaminobenzene and these acids in a hydrochloric medium in sealed tubes under pressure [10].



The 4-aminobenzimidazoles, as well as the analogous 5-amino derivatives obtained, were titrated potentiometrically. The basicity constants found are given in the Table.

Comparison of the Effect of the Amino Group on the Basicity of the Benzimidazole Ring

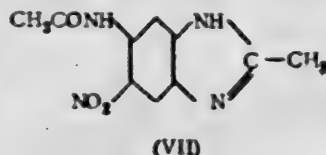
Expt. No.	Product studied	Basicity constant of the benzimidazole ring	Basicity constant of the amino group
1	Benzimidazole	10 ^{-8.6}	—
2	4-Aminobenzimidazole	10 ^{-8.7}	10 ^{-12.5}
3	5-Aminobenzimidazole	10 ^{-7.4}	10 ^{-10.7}
4	2-Methylbenzimidazole	10 ^{-8.8}	—
5	4-Amino-2-methylbenzimidazole	10 ^{-8.1}	10 ^{-12.3}
6	5-Amino-2-methylbenzimidazole	10 ^{-7.1}	10 ^{-11.2}
7	2-Benzylbenzimidazole	10 ^{-8.9}	—
8	4-Amino-2-benzylbenzimidazole	10 ^{-8.6}	10 ^{-11.9}
9	5-Amino-2-benzylbenzimidazole	10 ^{-7.6}	10 ^{-10.7}

As it is apparent from the Table, and as was expected, amino groups found in position 4, do not essentially effect the basicity constants of the benzimidazole derivative, while those in position 5, increase this constant by about 20 times. This means that the electron pair of the amino in position 5 is shifted considerably toward the imidazole ring, in contrast to the amino group in position 4, the electrons of which are

* The formyl derivative of 4-aminobenzimidazole and the free amine were very recently obtained and reported in the literature [6] and were patented in Switzerland and England as pharmaceuticals. Previously, Wooley [8] believed that he obtained and investigated 4-aminobenzimidazole; however, his belief was based on a major chemical error [6]. The author's investigation proceeded independently of the above.

not shifted in this direction. A logical conclusion from the above (if approximately equal effects of these amino groups on the benzene ring are assumed) must be that the amino group found in position 4 is more basic than that in position 5. This fact which initially seemed unexpected, meant that the above assumption of the approximate equality of the effects of these amino groups is untrue, and actually, the amino group in position 4 shows a much greater effect on the benzene ring than that in position 5. This conclusion was completely confirmed by the study of the nitration and azo coupling of reactions of derivatives of 4- and 5-aminobenzimidazole.

The nitration of 5-acetyl amino-2-methylbenzimidazole is reported in the literature [11]; it was shown that the nitro group enters exclusively into position 6 to form product (VII):

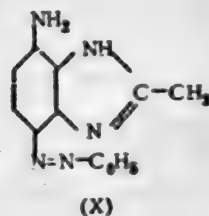
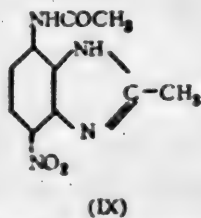
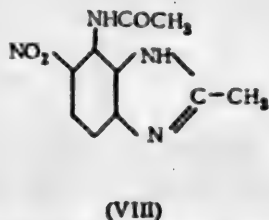


Not even traces of any other isomeric products are to be found. Previously [2], examining this reaction, it was shown on the basis of a series of facts, that its direction is not determined by the effect of the amino group which must direct mainly to position 4, but of the specifically greater reactivity of positions 5 and 6 in the benzimidazole molecule. This view found experimental verification in experiments on the coupling of 5-amino-benzimidazole and 5-amino-2-methylbenzimidazole with diazo compounds.

It was found that these substances were unable to couple, and even with the most active diazo compounds, only diazonium derivatives were formed, which were cleaved by mineral acids into the starting products.

Therefore, the amino group in position 5 of the benzimidazole ring is found in conjugation with the imidazole group which has only a slight effect on the benzene ring, insufficient to enable these compounds to participate in coupling reactions.

The nitration of 4-formaminobenzimidazole and 4-acetyl amino-2-methylbenzimidazole, reported in the previous communication [1], occurs very smoothly in concentrated sulfuric acid. As it was accurately shown, two isomeric mononitro compounds were formed in both cases, ortho (VIII) and para (IX), approximately in a ratio of 1:2.



It was found that 4-aminobenzimidazole and its derivatives readily participated in azocoupling. The diazo group entered exclusively in the p-position to the amino group (position 7) to form p-amino dyes (X).

Therefore, the data given, confirming the conclusion given on the basis of the results of potentiometric titration of the benzimidazole derivatives, show that an amino group in position 4 of benzimidazole has a great effect on the benzene ring of this compound; it activates it and even makes the azo coupling reaction possible. The substituent group enters mainly into the p-position to the amino group (position 7) which indicates the absence of interference in the conjugation between carbon atoms 5 and 6 in the 4-aminobenzimidazole derivative molecules. In spite of this, for some unexplained reason, the amino group in position 4 almost does not interact with the imidazole ring. All of the facts jointly create the impression that two systems of conjugation with little mutual interaction are present in molecules of 4-aminobenzimidazole derivatives: an aminobutadiene and an imidazole.

EXPERIMENTAL

4-Aminobenzimidazole

10 g of triaminobenzene was heated for an hour to reflux in a flask with 40 ml of 97% of formic acid. The

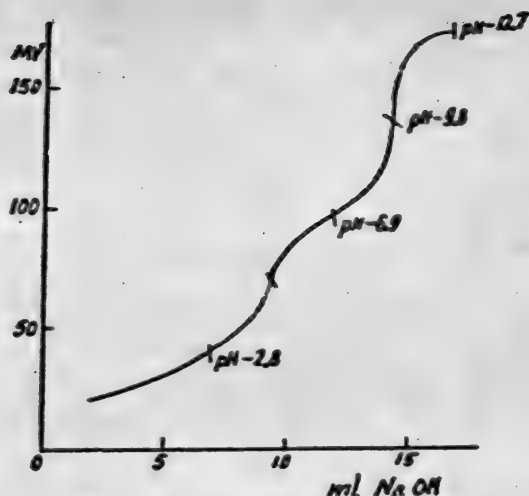


Fig. 1. Titration of 5-amino-2-methylbenzimidazole

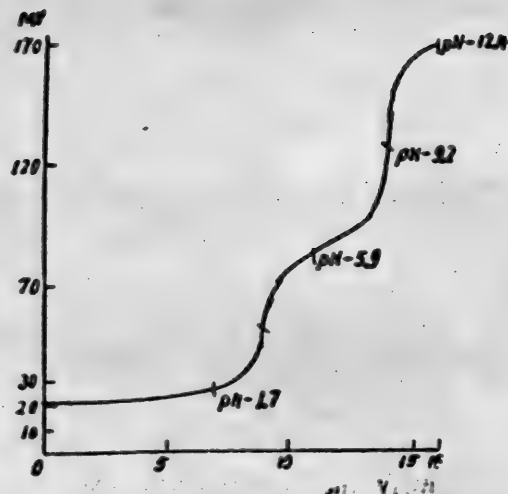


Fig. 2. Titration of 4-amino-2-methylbenzimidazole

tea-colored solution obtained was evaporated almost to dryness on the water bath, dissolved with heating in 50 ml of water, neutralized with ammonia, and after cooling, the almost white precipitate was filtered. The product was obtained chemically pure after one recrystallization from water with activated carbon. The yield of the formyl derivative of 4-aminobenzimidazole was 13 g, m.p. 172-174°.

0.1366 and 0.1422 g substance: 31.0 (22°, 762 mm) and 32.3 ml (23°, 760 mm) N_2 . Found %: N 26.3, 26.15. $C_8H_7ON_2$. Calculated %: N 26.08.

The saponification of the formyl derivative was effected by a 15 minute heating with 10-15% hydrochloric acid. The solution obtained was evaporated on the water bath until the start of crystallization, and after cooling, the precipitated 4-aminobenzimidazole hydrochloride was filtered. Dense, very slightly rose needles of the product were isolated in almost theoretical yield, and only traces of it remained in the mother liquor. The product did not have a sharp melting point. It was readily soluble in cold water, and free base precipitated as an oil by the addition of ammonia to the solution.

0.1020 g substance: 18.2 ml N_2 (22°, 754 mm). 0.1472 and 0.1513 g substance: 0.2062 and 0.2119 g AgCl. Found %: N 20.47; Cl 34.68, 34.64. $C_7H_7N_3 \cdot 2HCl$. Calculated: N 20.4; Cl 34.5.

4-Amino-2-methylbenzimidazole [5]

10 g of triaminobenzene was heated to reflux for 6-8 hours with 40 ml of glacial acetic acid. The almost black solution obtained was evaporated to dryness on the water bath, the residue dissolved in hot water, and precipitated with ammonia. After cooling, the product was filtered and recrystallized from water with active carbon. Yield 15 g. The product, the acetyl derivative of 4-amino-2-methylbenzimidazole, contained 2 molecules of crystallization water and melted widely at 93-100°.

The saponification of the acetyl derivative was effected in the same manner as in the previous case. The yield of the amine dihydrochloride was almost quantitative. The salt did not have a definite melting point, and was readily soluble in water; the free amine was obtained in the form of a tar by the action of ammonia.

4-Amino-2-phenylbenzimidazole

Experiments on the preparation of the above product by melting triaminobenzene with benzoic acid (1:2) at 180° led to the preparation of a substance not containing a free amino group and which was unchanged even after prolonged boiling with 15% hydrochloric acid. Evidently, triaminobenzene formed compound (V) containing 3 rings under these conditions, which was also confirmed by the results of elementary analysis.

0.1016, 0.1010 g substance: 12.9 ml N_2 (22°, 754 mm): 12.4 ml N_2 (20°, 754 mm). Found %: N 14.6, 14.2. $C_{13}H_{13}N_3$. Calculated %: N 14.2.

For this reason, 4-amino-2-phenylbenzimidazole was subsequently prepared by heating 2 g of triaminobenzene, 2 g of benzoic acid, and 5 ml of 15% hydrochloric acid to 180° in a sealed tube. The reaction mass was treated with ammonia, and the product which separated in the form of a tar, was removed and recrystallized from water with hydrochloric acid. The yield of the product, obtained in the form of colorless needles of the dihydrochloride, was 0.3 g. The salt did not have a sharp melting point.

The base, which crystallized from alcohol in the form of needles, melted sharply at 210-211°.

0.1010 g substance: 0.2772 g CO_2 , 0.0482 g H_2O . Found %: C 74.7; H 5.3. $C_{13}H_{13}N_3$. Calculated %: C 74.6; H 5.27.

4-Amino-2-benzylbenzimidazole

4 g of triaminobenzene and 4 g of phenylacetic acid were heated with 10 ml of 10% hydrochloric acid in a sealed tube at 180° for 2 hours. The reaction mixture was treated with ammonia, and the product precipitated in the form of an oil which rapidly solidified. It was recrystallized from water containing hydrochloric acid, and colorless shiny needles of the dihydrochloride were obtained. Yield 3.9 g, m.p. 242-248°, which was not very sharp.

0.1100 g substance: 13.8 ml N_2 (24°, 758 mm). 0.1456 and 0.1460 g substance: 0.1414 and 0.1415 g AgCl. Found %: N 14.37; Cl 24.05, 24.05. $C_{14}H_{13}N_3 \cdot 2HCl$. Calculated %: N 14.20; Cl 24.00.

The hydrochloride of the product was converted into the base by the action of an ammonia solution. The product was recrystallized from aqueous alcohol, M.p. 152-154°.

0.1376 g substance: 0.3804 g CO_2 ; 0.0687 g H_2O . 0.1076 and 0.1115 g substance: 17.8 ml N_2 (22°, 750 mm) and 18.6 ml N_2 (24°, 758 mm). Found %: C 75.30; H 5.54; N 19.10, 19.10. $C_{14}H_{13}N_3$. Calculated %: C 75.25; H 5.83; N 18.85.

Potentiometric Titration of the Amino Derivatives of Benzimidazole

The potentiometric titration of these compounds was conducted with a vacuum tube potentiometer of the system GIPKh with glass electrodes [12]. The values of the basic constants found are given in the theoretical part of the present communication.

Figs. 1 and 2 give the curves obtained upon the potentiometric titration of the isomeric amino-2-methylbenzimidazoles.

SUMMARY

Derivatives of 4-aminobenzimidazole were prepared by the condensation of consecutive triaminobenzene with organic acids, whose chemical properties were compared with those of the 5-aminobenzimidazoles. These products were studied by the method of potentiometric titration. The results obtained were compared with those of experiments on nitration and azo coupling of these substances.

It was shown that derivatives of 4-amino- and 5-aminobenzimidazole differ sharply from each other in chemical properties. Whereas the amino group in position 4 does not interact with the imidazole ring and strongly activates the benzene ring, that in position 5 greatly affects the imidazole ring and practically does not activate the benzene ring of these compounds.

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Received July 1, 1952

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*See Consultants Bureau English Translation p. 725.

SYNTHESIS OF γ -SUBSTITUTED PYRIDINES

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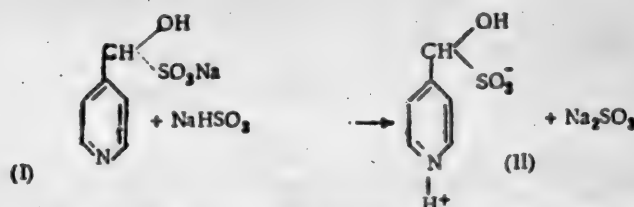
γ -Substituted pyridines are considered poorly accessible compounds because of difficulties connected with the isolation of pure γ -picoline which is contained in the β -picoline fraction along with δ -picoline and α,α -lutidine. However, these difficulties can be removed by using specific properties of the components of the β -picoline fractions. After the removal of α,α -lutidine readily accomplished with the aid of zinc chloride, it is fully possible, using the differences in reactivity of the methyl groups found in the δ - and γ -positions, to choose such conditions with which a differential reaction will proceed. In particular, the possibility of oxidizing γ -picoline to γ -formylpyridine in the presence of δ -picoline was of interest.

Up to now, there was no convenient method for the preparation of γ -formylpyridine [1] reported in the literature. Nevertheless, this compound is of considerable interest for the synthesis of a whole series of pyridine derivatives.

The experiments conducted showed that the differential oxidation of γ -picoline in the presence of δ -picoline was possible.

The properties of γ -formylpyridine were investigated, and the condensation reaction with malonic acid and ester was studied.

Upon treating a toluene solution of γ -formylpyridine with a 50% sodium bisulfite solution, a white finely crystalline powder precipitated which was a mixture of sodium γ -pyridylhydroxymethanesulfonate and sodium bisulfite. Upon the crystallization of the mixture obtained from water, white needle-like crystals not containing sodium and which were the internal salt of γ -pyridylhydroxymethanesulfonic acid, were formed. The formation of the internal salt occurs according to the scheme:



which was confirmed by the reaction of a specially prepared pure sodium γ -pyridylhydroxymethanesulfonate with an equimolecular amount of sodium bisulfite. An analogous transformation occurred by the action of acetic acid. The formation of an internal salt is also known for α -formylpyridine [2].

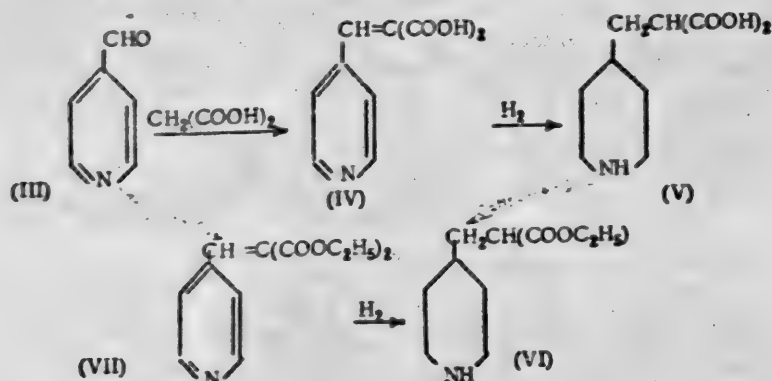
For the separation of the free aldehyde (III) the sodium γ -pyridylhydroxymethanesulfonate was heated for a short time with 35% potassium carbonate solution, extracted with ether or chloroform, and dried with potassium carbonate. If the solvent was distilled off, then a small amount of a sharp-smelling liquid with b.p. 185-187° remained, which rapidly crystallized in the air. The crystals were a compound of γ -formylpyridine with 1 mol. of water.

A considerable part of the aldehyde distilled together with the solvents, which could be detected by the addition of an alcoholic solution of hydrogen chloride to the distillate: the hydrochloride of γ -formylpyridine precipitated in the form of a white flocculant residue.

The hydrochloride crystallized with 0.5 mol. of water which could not be removed at 100° in vacuum. The anhydrous hydrochloride could only be obtained by vacuum distillation.

γ -Formylpyridine hydrochloride readily condensed with malonic acid and ester. The condensation with malonic acid proceeded in a glacial acetic acid medium at 85-90° with the formation of 4-(β,β -dicarboxylvinyl)pyridine (IV). The condensation with malonic ester proceeded in a pyridine medium in the presence of a small

excess of piperidine (2-3% over the equimolecular amount) with the formation of 4-(β,β -dicarbethoxyvinyl)pyridine (VII). The reaction occurred in the cold upon prolonged standing. Heating did not accelerate the process or increase the yield.



4-(β,β -Dicarboxyvinyl)pyridine (IV) was partly decarboxylated by heating with an alcoholic hydrogen chloride solution, which was shown by the precipitation of ethyl β -(pyridyl-4)-acrylate from the reaction mixture. For this reason, 4-(β,β -dicarbethoxyvinyl)pyridine (VII) could not be obtained by esterification. (VII) also could not be obtained by means of the acid chloride, since thionyl chloride reacted with 4-(β,β -dicarboxyvinyl)pyridine only at 70-75°, at which a partial decarboxylation occurred.

Much more stable is 4-(β,β -dicarboxyethyl)piperidine (V) which was readily obtained by the hydrogenation of (IV) hydrochloride in 4% hydrochloric acid in the presence of a platinum catalyst (according to Adams).

4-(β,β -dicarbethoxyethyl)piperidine (VI) was formed in good yield by the esterification of (V). Hydrogenation of (VII) over a platinum catalyst in absolute alcohol also led to the formation of (VI). The latter compound was converted into 2-quinuclidinecarboxylic acid by means of the corresponding bromo derivative [3].

EXPERIMENTAL

Isolation of the Internal Salt of γ -Pyridylhydroxymethanesulfonic acid (II).

10 ml of a 50% sodium bisulfite solution was added to a toluene solution of 2.42 g of γ -formylpyridine, obtained by the oxidation of γ -picoline, cooled to 0°, stirred until the formation of mushy mass on the bottom of the beaker, the liquid poured from it, and the residue added to 50 ml of alcohol. It was thoroughly mixed and filtered. The residue was washed with alcohol, ether, and air dried. 7.3 g of a white crystalline powder was obtained which was a mixture of sodium γ -pyridylhydroxymethanesulfonate and sodium bisulfite.

Upon recrystallization from water, white, shiny, needlelike crystals of the internal salt of γ -pyridylhydroxymethanesulfonic acid were obtained. The substance is readily soluble in hot water, moderately in the cold; it is insoluble in the common organic solvents and does not melt.

3.470 mg substance: 4.831 mg CO_2 ; 1.247 mg H_2O . 6.371 mg substance: 3.37 ml 0.01 N H_2SO_4 .

0.1615 g substance: 0.1910 g BaSO_4 . Found %: C 37.99; H 4.02; N 7.41; S 16.85. $\text{C}_6\text{H}_7\text{O}_4\text{NS}$.

Calculated %: C 38.09; H 3.70; N 7.40; S 16.93.

Conversion of the Internal Salt of γ -Pyridylhydroxymethanesulfonic Acid into the Sodium Salt and the Reverse.

2.25 ml of a 1N solution of sodium hydroxide was added to 0.56 g of the internal salt of γ -pyridylhydroxymethanesulfonic acid, 50 ml of absolute alcohol was added to the solution formed, and shaken. The precipitated residue was filtered, washed with ether, and dried in vacuum. Weight of the residue, 0.59 g. Yield, 95% of the theoretical.

0.1049 g substance: 0.1199 g BaSO_4 . 0.1044 g substance: 0.0325 g Na_2SO_4 . Found %: S 15.69; Na 10.91. $\text{C}_6\text{H}_7\text{O}_4\text{NSNa}$. Calculated %: S 15.16; Na 10.90.

0.17 g of dry sodium bisulfite, freshly precipitated from a 50% alcoholic solution with alcohol, was added to 0.33 g of sodium γ -pyridylhydroxymethanesulfonate obtained from the internal salt. The mixture was recrystallized from water. The precipitate was washed with alcohol and ether, and dried in vacuum at 120°. 0.25 g of the substance was obtained. Yield, 85% of the theoretical.

3.563 mg substance: 4.940 mg CO₂; 1.316 mg H₂O. 6.834 mg substance: 3.47 ml 0.01 N H₂SO₄.
Found %: C 37.83; H 4.13; N 7.10. C₆H₅O₄NS. Calculated %: C 38.09; H 3.70; N 7.40.

γ-Formylpyridine Thiosemicarbazone

If the toluene filtrate, containing 3.1 g of γ-formylpyridine was stirred for one hour with a solution of 2.63 g of thiosemicarbazide in 13 ml of water at 70-75°, a greenish crystalline precipitate with m.p. 213-214° formed. The residue was poorly soluble in alcohol, insoluble in water, acetone, and ether. Yield 5 g or 96 % of the theoretical. After recrystallization from alcohol, the substance melted at 215-217° with decomposition [4].

6.135 mg substance: 7.971 mg BaSO₄. Found %: S 17.84. C₇H₅N₄S. Calculated %: S 17.78.

Upon treating the thiosemicarbazone with 10% hydrochloric acid, a bright yellow precipitate which was the thiosemicarbazone hydrochloride, melted at 238.5-239.5° after recrystallization from 50% alcohol. If dissolved in cold water at a ratio of 1:90, it was precipitated from the solution with an excess of hydrochloric acid.

0.2262 g substance: 0.2402 g BaSO₄. Found %: S 14.58. C₇H₅N₄S·HCl. Calculated %: S 14.78.

Isolation of Free γ-Formylpyridine (III)

7.6 g of the impure sodium salt of γ-pyridyl hydroxymethanesulfonic acid was heated on the water bath for 5 minutes with 15 ml of water and 30 ml of a 50% potassium carbonate solution. The precipitate went into solution, and the sharp characteristic odor appeared.

The hot solution was rapidly extracted with chloroform (in ether, the aldehyde is less soluble). The chloroform extract was dried with potassium carbonate and evaporated in vacuum. 1.56 g of a colorless, mobile liquid remained which distilled at 185-187° and was γ-formylpyridine. The compound obtained was characterized by its volatility, and a considerable amount is transferred into the distillate upon evaporation of the solution.

γ-Formylpyridine rapidly absorbed moisture from the air and was converted into a crystalline compound melting at 58-60°. The crystallohydrate dissolves readily in water and alcohol, less in ether.

3.990 mg substance: 8.481 mg CO₂; 2.267 mg H₂O. 4.752 mg substance: 10.103 mg CO₂; 2.371 mg H₂O.
4.308 mg substance: 4.34 ml 0.01 N H₂SO₄. 5.912 mg substance: 4.80 ml 0.01 N H₂SO₄. Found %:
C 57.96, 57.98; H 5.82, 5.58; N 11.44, 11.38. C₆H₅ON·H₂O. Calculated %: C 57.60; H 5.60; N 11.20.

2.09 g of γ-formylpyridine hydrochloride was formed from the chloroform distillate by means of an alcoholic solution of hydrogen chloride. The total yield, based on the sodium salt of γ-pyridylhydroxymethanesulfonic acid, was 78% of the theoretical. γ-Formylpyridine hydrochloride was a white powder, readily soluble in water and alcohol, poorly in chloroform, and insoluble in ether. It contained 0.5 mol. of water. M.p. 132-134°.

5.800 mg substance: 0.469 ml N₂ (25°, 730.5 mm). 5.143 mg substance: 0.422 ml N₂ (25°, 730.5 mm).
4.597 mg substance: 4.381 mg AgCl. 5.989 mg substance: 5.702 mg AgCl. Found %: N 8.90, 9.03;
Cl 23.59, 23.55. C₆H₅ON·HCl·0.5 H₂O. Calculated %: N 9.18; Cl 23.28.

γ-Formylpyridine hydrochloride was distilled in vacuum upon heating and lost its water of crystallization. The anhydrous hydrochloride melted at 159.5-161.5°. However, it rapidly absorbed water and was again converted into the compound with m.p. 132-134°.

8.00 mg substance: 0.684 ml N₂ (21°, 728.5 mm). Found %: N 9.52. C₆H₅ON·HCl. Calculated %: N 9.75.

4-(β,β-Dicarboxyvinyl)pyridine (IV)

3.1 g of γ-formylpyridine hydrochloride, 2.26 g of malonic acid, and 7.5 ml of glacial acetic acid were heated with stirring on the water bath to 85-90°. Everything went into solution at 40-50°, while at 80-85°, a precipitate began to form. It was stirred at 85-90° for 45 minutes, filtered, washed with glacial acetic acid and then with ether, and air dried. 3.8 g of 4-(β,β-dicarboxyvinyl)pyridine hydrochloride with m.p. 219-220° was obtained. Yield 81% of the theoretical. The substance was soluble in water, and insoluble in alcohol, ether, and acetic acid.

3.448 mg substance: 5.993 mg CO₂; 1.133 mg H₂O. 3.619 mg substance: 2.278 mg AgCl. 6.289 mg substance:
3.906 mg AgCl. Found %: C 47.40; H 3.67; Cl 15.57, 15.37. C₆H₅O₄N·HCl. Calculated %: C 47.05; H 3.48;
Cl 15.47.

In order to separate the free 4-(β,β-dicarboxyvinyl)pyridine, the hydrochloride was mixed with an equivalent amount of sodium acetate in aqueous solution. The precipitate which came out was filtered, washed with water, alcohol, and ether, and air dried.

4-(β,β -Dicarboxyvinyl)pyridine was not soluble in water or in the usual organic solvents. M.p. 263-265° (with decomposition). It crystallized with 1.5 mol. of water.

7.533 mg substance: 3.50 ml 0.01 N H_2SO_4 . 5.640 mg substance: 2.61 ml 0.01 N H_2SO_4 . Found %: N 6.54, 6.46. $\text{C}_7\text{H}_7\text{O}_4\text{N} \cdot 1.5\text{H}_2\text{O}$. Calculated %: N 6.36.

Upon drying in vacuum at 100°, 4-(β,β -dicarboxyvinyl)pyridine loses its crystallization water.

4.936 mg substance: 2.58 ml 0.01 N H_2SO_4 . 3.126 mg substance: 1.62 ml 0.01 N H_2SO_4 . Found %: N 7.32, 7.25. $\text{C}_7\text{H}_7\text{O}_4\text{N}$. Calculated %: N 7.25.

4-(β,β -Dicarboxyethyl)piperidine (V).

A solution of 4-(β,β -dicarboxyvinyl)pyridine hydrochloride in 50 ml of hydrochloric acid was hydrogenated at room temperature in the presence of 0.3 g of platinum oxide at 40-60 mm of water pressure. The absorption was completed in 5-6 hours. The catalyzate was filtered, washed with a small amount of distilled water, filtered, evaporated in vacuum at 30° until a slurry was obtained, the residue filtered, washed with absolute alcohol and ether, and dried in a vacuum desiccator. Coarse, shiny, colorless crystals with m.p. 237-239° were obtained in a 3.27 g quantity. Yield 91% of the theoretical. The substance was readily soluble in water, difficultly in alcohol, and insoluble in ether.

3.072 mg substance: 5.128 mg CO_2 ; 1.871 mg H_2O . 5.032 mg substance: 5.030 mg AgCl. Found %: C 45.52; H 6.81; Cl 14.90. $\text{C}_9\text{H}_{15}\text{O}_4\text{N} \cdot \text{HCl}$. Calculated %: C 45.47; H 6.74; Cl 14.94.

In order to separate the free 4-(β,β -dicarboxyethyl)piperidine, the hydrochloride was mixed with an equivalent amount of sodium acetate and a small amount of water. The residue obtained was washed with water, alcohol, and ether, and dried in a vacuum desiccator. 4-(β,β -Dicarboxyethyl)piperidine was obtained in the form of white fine crystals with m.p. 255.5-256° (with decomposition). The substance was readily soluble in water.

5.247 mg substance: 2.50 ml 0.01 N H_2SO_4 . Found %: N 6.67. $\text{C}_9\text{H}_{15}\text{O}_4\text{N}$. Calculated %: N 6.96.

4-(β,β -Dicarbethoxyethyl)piperidine (VI).

8 g of 4-(β,β -dicarboxyethyl)piperidine hydrochloride was heated with 80 ml of a 4% alcoholic solution of hydrogen chloride for 2 hours with boiling, and the alcohol was then removed in vacuum. The residue was heated with a fresh portion of 4% alcoholic hydrogen chloride solution for 2 hours more, the alcohol removed in vacuum, the residue treated with an excess of a 50% potassium carbonate solution, and extracted with ether. The ether extract was dried with potassium carbonate, filtered, and treated with an alcoholic solution of hydrogen chloride to a weakly acid solution on Congo. The precipitated shiny residue was filtered, washed with ether, and dried in a vacuum desiccator. 7.8 g of 4-(β,β -dicarbethoxyethyl)piperidine hydrochloride with m.p. 128-129° [3] was obtained. Yield 79.5% of the theoretical. The substance was readily soluble in water, alcohol, chloroform, and insoluble in ether.

3.805 mg substance: 7.448 mg CO_2 ; 2.665 mg H_2O . 3.841 mg substance: 7.516 mg CO_2 ; 2.654 mg H_2O . 7.147 mg substance: 2.52 ml 0.01 N H_2SO_4 . Found %: C 53.38, 53.37; H 7.84, 7.73; N 4.94. $\text{C}_{11}\text{H}_{23}\text{O}_4\text{N} \cdot \text{HCl}$. Calculated %: C 53.15; H 7.80; N 4.77.

4-(β,β -Dicarbethoxyvinyl)pyridine (VII)

3.3 g of γ -formylpyridine ester, 3.53 g of malonic ester 8.6 ml of pyridine, and 3.3 ml of piperidine, were left to stand in a closed flask for 4 days at room temperature (about 15°). The precipitated residue of piperidine hydrochloride was filtered, the filtrate was evaporated in vacuum at 50°, the residue was diluted with 60 ml of dry ether, the precipitated piperidine hydrochloride was filtered once, the ether filtrate was washed with 15% sodium carbonate solution, and dried with potassium carbonate. The ether was removed, and the residue was vacuum distilled, collecting the fraction with b.p. 176-178° at 7 mm. Yield 3.3 g or 62% of the theoretical.

In order to prepare the hydrochloride, the compound obtained was dissolved in absolute ether, and a solution of hydrogen chloride in alcohol added to a weakly acidic reaction on Congo. 3.6 g of a substance with m.p. 180-182° [3] was obtained after many recrystallizations from alcohol. The yield of the hydrochloride based on the ether was 97% of the theoretical.

7.221 mg substance: 2.49 ml 0.01 N H_2SO_4 . 7.140 mg substance: 2.15 ml 0.01 N H_2SO_4 . 3.948 mg substance: 2.101 mg AgCl. Found %: N 4.82, 4.90; Cl 12.53. $\text{C}_{11}\text{H}_{15}\text{O}_4\text{N} \cdot \text{HCl}$. Calculated %: N 4.90; Cl 12.42.

4-(β,β -Dicarboethoxyethyl)piperidine [3] was obtained by the hydrogenation of 4-(β,β -dicarboethoxyvinyl)pyridine hydrochloride in absolute alcohol over platinum oxide.

SUMMARY

A series of γ -formylpyridine derivatives was prepared and their condensation with malonic acid and ester was studied.

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Received February 12, 1953

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* See Consultants Bureau English Translation, p. 733.



SYNTHESES BASED UPON ANABASINE

V. STUDY OF THE TRANSFORMATION PRODUCTS OF N-(β -HYDROXYETHYL)ANABASINE

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The synthesis of anabasine amino alcohols and the transformations of N-(β -hydroxyethyl)anabasine were reported in the previous communications [1, 2]. The experimental data of the chemical characteristics of N-(β -hydroxyethyl)anabasine, and the products of its transformation are given in the present communication.

Reagents: anabasine, 16 g, ethylene oxide, 4.35 g.
Reaction conditions: temperature, 18-20°, volume of solvent, 50 ml.

Solvent	Experiment time (in hrs.)	Yield of N-(β -hydroxyethyl)anabasine (in %)	Amount of anabasine recovered (in %)
Methyl alcohol	24	36	57
Methyl alcohol	48	39.8	50
Methyl alcohol	96	43	29
Absolute ethyl alcohol	24	40	55
" " "	36	47	47
" " "	48	59	26
" " "	96	70	13

The anabasine (I) used for the investigation was obtained and purified as reported previously [3]. The reaction of anabasine with ethylene oxide was accomplished at room temperature in methyl and ethyl alcohol solutions at various reaction times, with the reagents used in equimolecular amounts. The results obtained are given in the Table.

As is apparent from the data given, better yields of N-(β -hydroxyethyl)anabasine (II) were obtained in absolute alcohol with a reaction time of 96 hours.

N-(β -Hydroxyethyl)anabasine was characterized by the preparation of salts: the hydroiodide with m.p. 204-205°, the hydrochloride with m.p. 193-194°, the picrate with m.p. 180-181°, the phenylmethane with m.p. 143-144°, and the acetyl derivative [4].

During a study of the dehydration reaction of N-(β -hydroxyethyl)anabasine with phosphoric anhydride, a crystalline product with m.p. 53-54° was isolated containing condensed lupinine and pyridine rings. The new compound was called 4,5-(α, β -pyridylene)norlupinane (III). It was readily soluble in organic solvents (ether, chloroform, benzene), and more poorly, in water. It gives a crystalline picrate with m.p. 201-202°.

A series of experiments showed that the optimum temperature conditions for the dehydration of N-(β -hydroxyethyl)anabasine with phosphoric anhydride lie within the limits 120-130° (Yield 16.5%). Below 120°, the reaction did not occur. Above 140°, the reaction proceeds with strong tarring, which is, evidently, due to the polymerization of vinylianabasine formed during the reaction process.

The structure of 4,5-(α, β -pyridylene)norlupinane (III) was proved by its oxidation with potassium permanganate; a dibasic acid was isolated with m.p. 229-230°. A study of the properties of this acid (IV) [5] and its anhydride (V) [6], made it possible to conclude quinolinic acid was formed by this reaction. A direct comparison of the acid with the quinolinic acid obtained by the oxidation of quinoline showed their identity.

The formation of quinolinic acid during the oxidation of 4,5-(α, β -pyridylene)norlupinane showed that during the dehydration of N-(β -hydroxyethyl)anabasine with phosphoric anhydride the ring closure occurs by means of the hydroxyl of the side chain and the hydrogen of α -carbon atom of the pyridine ring.

The preparation of N-(β -hydroxyethyl)anabasine and its chemical transformations can be represented by the following scheme:

1.532 mg substance: 0.178 ml N_2 (25°, 723 mm). 2.426 mg substance: 0.262 ml N_2 (28°, 723 mm).
Found %: N 9.09, 8.60. $C_7H_5O_4N$. Calculated %: N 8.38.

11.015 mg acid: 1.33 ml 0.1 N NaOH. 8.368 mg acid: 1.03 ml 0.1 N NaOH. Found: Equivalent
84.7, 83.1. $C_7H_5O_4N$. Calculated: Equivalent 83.5.

Acid anhydride. 62 mg of the finely ground quinolinic acid obtained by the oxidation of N-(β -hydroxyethyl)anabasine in 200 mg of acetic anhydride was heated on an oil bath at 120-125° until complete solution of the acid. Then after a short heating at 150°, the reaction product was cooled and dissolved in carbon tetrachloride. On standing, slow precipitation of a crystalline product started in the solution. On the following day, the crystals were filtered and washed with carbon tetrachloride. Crystals in the form of shiny prisms with m.p. 133-134° were obtained after drying. Upon heating the anhydride with resorcin on the water bath, a yellow fluorescent color was obtained. This is a characteristic reaction for quinolinic anhydride (V).

SUMMARY

1. The reaction of equimolar amounts of anabasine and ethylene oxide in methyl and absolute ethyl alcoholic media was studied. The best yields (69%) of N-(β -hydroxyethyl)anabasine were obtained by conducting the reaction in absolute alcohol at room temperature for 96 hours.

2. The hydroiodide with m.p. 204-205°, the hydrochloride with m.p. 193-194°, the picrate with m.p. 180-181°, and the phenylurethane with m.p. 143-144° were prepared to characterize the N-(β -hydroxyethyl)anabasine.

3. The dehydration reaction of N-(β -hydroxyethyl)anabasine by phosphoric anhydride was studied. A new compound called 4,5-(α,β -pyridylene)norlupinane (III) was obtained. The structure of this compound was proved by oxidation to quinolinic acid and the preparation of the anhydride of the latter. It was shown that the dehydration of N-(β -hydroxyethyl)anabasine occurs by means of the hydroxyl group of the alcohol and the hydrogen of the α -position of the pyridine ring.

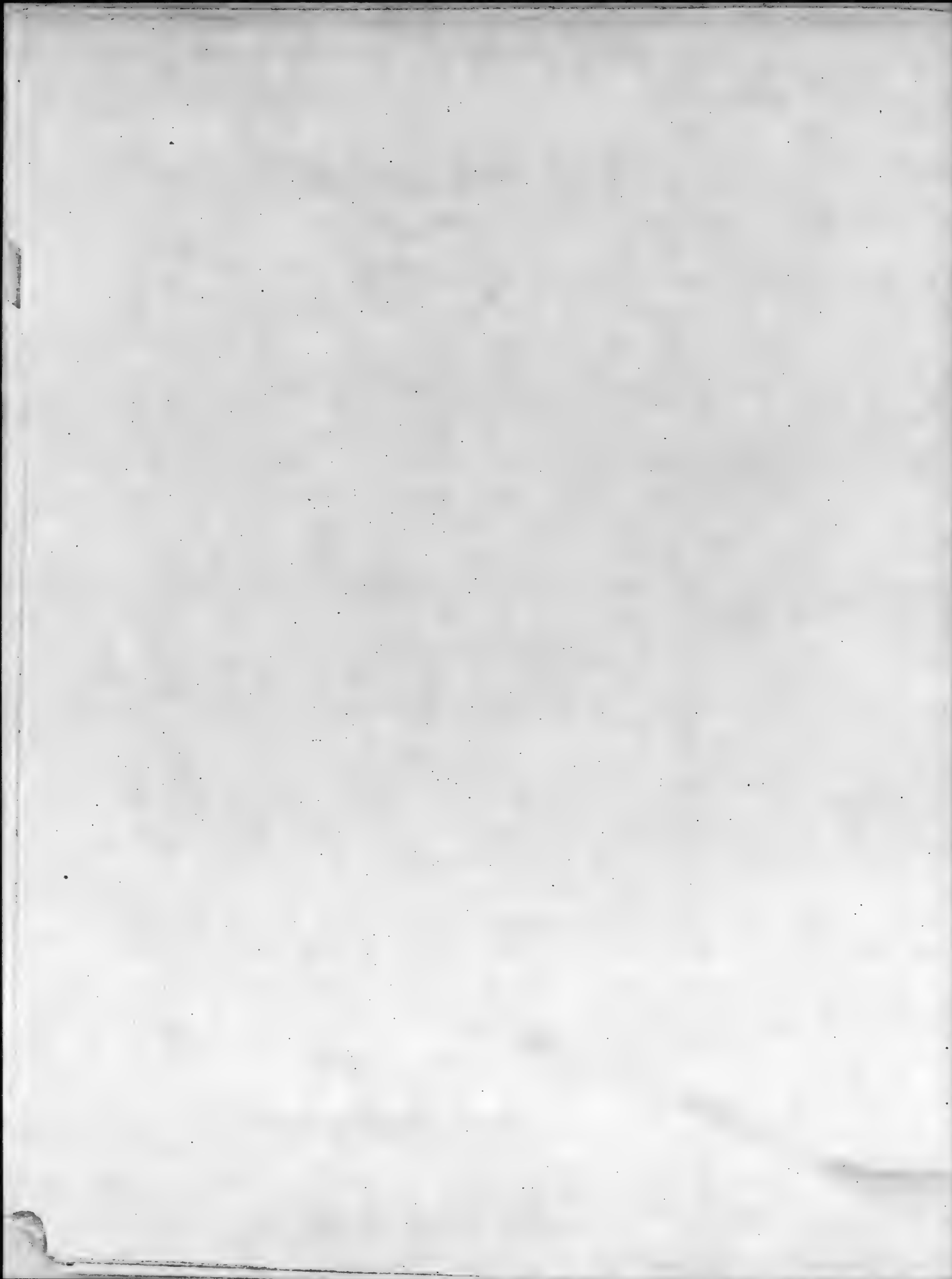
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Received September 8, 1952.

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* See Consultants Bureau Translation, p. 2135.



SYNTHESIS OF N,O-PEPTIDES OF SERINE

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In relation to the study of the role of the hydroxyl in proteins, it was found necessary to synthesize peptides of serine, not only with the amino, but also with the hydroxyl group.

More than once it has been suggested in the literature that ester linkages existed in proteins, or more accurately, in systems of proteins [1]. But this suggestion has only been a hypothesis up to now, unproved experimentally. For the experimental solution of this problem, it was necessary to initially study the properties of ester linkages formed by aminoacids and the hydroxyl groups of β -hydroxyamino acids.

For this purpose, methods of synthesis were developed during the present investigation and a series of N,O-peptides of serine was obtained.

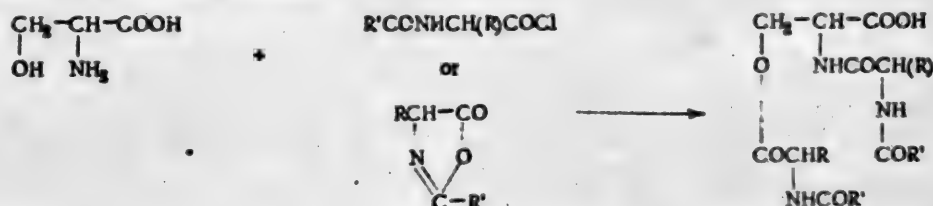
The N,O-peptides are considered to be those formed by the amino and hydroxyl groups of β -hydroxyamino acids.

The number of synthesized peptides of β -hydroxyamino acids is very small [3]. The first peptide of threonine was first synthesized in 1950 [2], while the N,O-peptides are scarcely studied. In the majority of cases, they have only been obtained as side products during the synthesis of peptides of hydroxyamino acids.

Thus in 1927, N,O-di(acetyldehydrophenylalanyl)serine was obtained during the condensation of serine with 2-methyl-4-benzal-5-oxazolone in addition to the N-peptide, which was not studied further by the authors [3].

N,O-dityrosylserine was obtained in 1932 [4], and in 1949, at the conclusion of the present investigation, a communication appeared on the synthesis of the ethyl ester of O-(N-benzoylphenylalanyl)-N-benzoylserine [5]. These concluded the investigations on N,O-peptides of β -aminohydroxy acids.

The reaction between acylated amino acid halides and oxazolones of serine and its derivatives was used for the synthesis of N,O-peptides of serine:



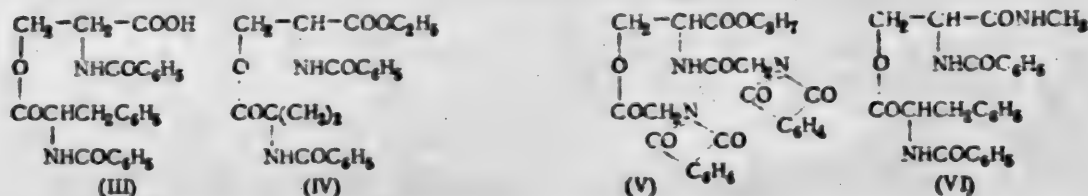
Initially, the above reaction was applied to the condensation of 2-methyl-4-benzal-5-oxazolone with serine. The yield of N,O-diacetyldehydrophenylalanylserine (I) was increased by varying several of the reaction conditions. The latter compound was hydrolyzed by hydrogen over palladium. N,O-diacetylphenylalanylserine (II) was first obtained by the authors as a result:



However, this method was limited by the poorly accessible unsaturated oxazolones with aliphatic radicals in the 4-position and the many stages in the synthesis. For this reason, investigations were conducted on the synthesis of N,O-peptides of serine with acylated amino acid halides and saturated oxazolones.

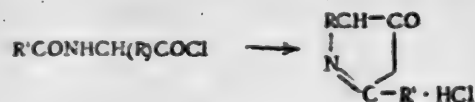
The first experiments conducted in this direction, led to negative results [6]: hippurylchloride did not react with benzoylserine or benzoylthreonine in ether and benzene media.

After varying the experimental conditions, in particular, the conducting of the experiments in homogenous medium, the following N,O-peptides and N-acyl-O-peptides of serine were synthesized: O-(benzoylphenylalanyl)-N-benzoylserine (II), by the action of N-benzoylphenylalanyl chloride on benzoylserine, yield 40%; the ethyl ester of O-(benzoylaminoisobutyryl)-N-benzoylserine (IV), by the action of N-benzoylaminoisobutyryl hydrochloride on the ethyl ester of N-benzoylserine, yield 18%; the isopropyl ester of N,O-diphthalylglycylserine (V), by the action of N-phthalylglycyl chloride on the isopropyl ester of serine, yield, 69%; and the methylamide of O-(benzoylphenylalanyl)-N-benzoylserine (VI), by the action of N-benzoylphenylalanylchloride on the methyl amide of N-benzoylserine, yield 77%.



In addition to the acylated amino acid chlorides, the corresponding oxazolones were also used. But these oxazolones react much less readily with serine and its derivatives, and N,O-peptides could not be obtained in these cases. Thus, for example, benzoylserine reacted with benzoylphenylalanyl chloride to form O-(benzoylphenylalanyl)-N-benzoylserine. The reaction did not occur with 2-phenyl-4-benzyl-5-oxazolone. The Table gives the experiments conducted. They prove the above-mentioned facts that oxazolones react less readily than acylated amino acid chlorides. The latter also react non-uniformly.

Now it can be considered proved that acyl amino acid chlorides spontaneously are transformed into oxazolone hydrochlorides, which are also capable of reacting with amine and hydroxyl groups:



Evidently, acylated amino acid chlorides are much more reactive than oxazolone hydrochlorides. This is particularly shown by the fact that phthalylglycyl chloride, which cannot be transformed into the salt of oxazolone, reacted exceptionally readily with serine.

The N,O-peptides obtained in the present investigation were subjected to the action of fermenta. The results are reported in another communication [7].

Reaction of Serine and its Derivatives with Acylated Amino Acid Chlorides and Oxazolones.

Names of the reaction components		Reaction products
1	2	3
Serine	2-Methyl-4-benzal-5-oxazolone	N,O-di-(acetyldehydrophenylalanyl)serine
Isopropyl ester of serine (hydrochloride)	Phthalylglycyl acid chloride	Isopropyl ester of N,O-di-(phthalylglycyl)serine
Benzoylserine	2-Phenyl-4-benzyl-5-oxazolone	Reaction did not occur
Benzoylserine	Benzoylphenylalanyl acid chloride	O-(benzoylphenylalanyl)-N-benzoylserine
Ethyl ester of benzoylserine	2-Phenyl-4,4-dimethyl-5-oxazolone	Reaction did not occur
Ethyl ester of benzoylserine	Benzoylaminoisobutyryl acid chloride	Ethyl ester of O-(benzoylaminoisobutyryl)-N-benzoylserine
Methylamide of benzoylserine	Benzoylphenylalanyl acid chloride	Methylamide of O-(benzoylphenylalanyl)-N-benzoylserine

EXPERIMENTAL

Synthesis of N,O-di-(acetylphenylalanyl)serine (II)

a) Preparation of N,O-di-(acetyldehydrophenylalanyl)serine (I) 9.35 g of 2-methyl-4-benzal-5-oxazolone

dissolved in 65 ml of acetone was added to a solution of 5.25 g of serine in 42 ml of 1.2 N alkali. The mixture was shaken for 3 hours, the undissolved oxazolone was filtered off, and the filtrate was evaporated in vacuum. The oil which precipitated at the start of the evaporation was separated (substance A). The filtrate was evaporated to dryness in vacuum (substance B).

Substance A crystallized upon standing. The crystals obtained were treated with boiling benzene, and then recrystallized from aqueous alcohol. N,O-Di-(acetaldehydophenylalanyl)serine with m.p. 196° was obtained. According to literature data, m.p. 202° [3].

Substance B (6.6 g) was dissolved in absolute alcohol for separation from sodium chloride. The filtrate was evaporated to half of its volume and filtered once more. After evaporation to dryness, a substance remained which was in the form of light yellow shiny platelets. It was dissolved in a mixture of alcohol and ethyl acetate and precipitated with petroleum ether. N-(Acetyldehydrophenylalanyl)serine with m.p. 173° was obtained. According to literature data, m.p. 178° [3].

Found: equiv. 328, 324. Calculated: equiv. 292.

b) Hydrogenation of N,O-di-(α -acetyldehydrophenylalanyl)serine. 2.8 g of N,O-di-(α -acetyldehydrophenylalanyl)serine was dissolved in absolute methyl alcohol and hydrogenated with hydrogen over palladium black for 18 hours. 275 ml of hydrogen were absorbed (theoretical amount 262 ml). The solution was evaporated in a vacuum after the removal of the catalyst. The oil which precipitated crystallized upon strong cooling and prolonged standing. N,O-Di-(α -acetylphenylalanyl)serine melted at 82-85°. Yield 2.25 g, 79.8% of the theoretical.

The compound has not been reported in the literature.

Found %: C 60.70, 60.53; H 6.48, 6.43; N 8.67, 8.56. $C_{23}H_{29}O_7N_3 \cdot \frac{1}{2}H_2O$. Calculated %: C 60.97; H 6.09; N 8.53.

After drying in vacuum at 80° (5 mm) over phosphoric anhydride, m.p. 103-105°.

Found %: C 61.67, 61.58; H 6.17, 6.18; N 8.72, 8.72. $C_{23}H_{29}O_7N_3$. Calculated %: C 62.11; H 6.09; N 8.69.

c) Preparation of N-(acetylphenylalanyl)serine. 2 g of N-(acetyldehydrophenylalanyl)serine in methyl alcohol solution was hydrogenated for 5 hours with hydrogen over palladium black. 210 ml of hydrogen was absorbed (theoretical amount 196 ml). After the removal of the catalyst and washing with alcohol, the filtrate was concentrated in vacuum. The substance solidified in the form of shiny scales.

M.p. 76-78°. Yield of N-(acetylphenylalanyl)serine was 1.9 g, 95% of the theoretical.

The substance was dried in vacuum at 56° over phosphoric anhydride.

Found %: C 54.72, 54.59; H 6.28, 6.24; N 8.85, 8.88. $C_{14}H_{19}O_3N_2 \cdot \frac{1}{2}H_2O$. Calculated %: C 55.47; H 6.27; N 9.20.

Reaction of the Ethyl Ester of N-Benzoylserine with 2-Phenyl-4,4-dimethyl-5-oxazolone

A solution of 0.24 g of the ethyl ester of N-benzoylserine (m.p. 85°) and 0.27 g of 2-phenyl-4,4-dimethyl-5-oxazolone in absolute toluene were heated for 3 hours at 65-70° and for 3 hours at the boiling point of toluene. The toluene was removed in vacuum and aniline was added to the residue to remove the unreacted oxazolone. After a 5 minute heating, at 50-60°, the reaction mass solidified. The residue, recrystallized from benzene, was benzoyl-aminoisobutyric acid anilide (0.3 g). M.p. 227°.

The aniline was removed from the mother liquor with hydrochloric acid, and benzoylserine ethyl ester was isolated. Therefore, the reaction between the ethyl ester of N-benzoylserine and 2-phenyl-4,4-dimethyl-5-oxazolone did not occur.

Synthesis of the Ethyl Ester of O-(Benzoylaminoisobutyryl)-N-Benzoylserine (IV)

2g of N-benzoylserine ester and 2.25 g of benzoylaminoisobutyryl acid chloride in chloroform solution were heated for 8 hours on the water bath at 60-65°. The undissolved residue was filtered off, and the filtrate evaporated in vacuum. The residual oil was dissolved in alcohol, and water was added dropwise to the solution until a cloudiness appeared. The ethyl ester of O-(benzoylaminoisobutyryl)-N-benzoylserine was isolated in the form of long white needles. Yield 0.5 g. M.p. 128°.

The compound has not been reported in the literature.

Found %: C 65.40, 65.49; H 6.14, 6.14; N 6.75, 6.83. $C_{23}H_{25}O_6N_2$. Calculated %: C 65.40; H 6.16; N 6.63.

Hydrolysis of the Ethyl Ester of O-(Benzoylaminoisobutyl)-N-benzoylserine (IV). The amounts of the substances given below were treated with 8 ml of 1/40 N alkali and boiled on the water bath for 3 hours. 8 ml of 1/40 N hydrochloric acid was added to the hydrolyzate, and the excess of the latter was back titrated.

32.8 mg substance: 6.12 ml 1/40 N NaOH. 22.1 mg substance: 4.10 ml 1/40 N NaOH. $C_{23}H_{25}O_6N_2$.
Calculated: 6.11 ml 1/40 N NaOH. 4.10 ml 1/40 N NaOH.

Reaction of N-Benzoylserine with 2-phenyl-4-benzyl-5-oxazolone

2-Phenyl-4-benzyl-5-oxazolone was prepared from benzoylphenylalanine and acetic anhydride. M.p. 69°. 1 g of N-benzoylserine in dioxane was mixed with a solution of 1.5 g of oxazolone in chloroform. The mixture was heated for 6 hours to gentle boiling. The chloroform and dioxane were removed in vacuum, and the residual oil was dissolved in absolute benzene. Upon standing, crystals of N-benzoylserine (0.87 g) precipitated slowly. A mixed sample with an N-benzoylserine preparation did not give a depression in melting point. Therefore, the reaction between benzoylserine and 2-phenyl-4-benzyl-5-oxazolone did not occur.

Synthesis of O-(Benzoylphenylalanyl)-N-benzoylserine (II)

A solution of 3.0 g of benzoylserine in dioxane was added to a chloroform solution of the acid chloride obtained from 4.0 g of benzoylphenylalanine. The mixture was boiled for 6 hours, concentrated in vacuum, and the residual oil dissolved in absolute benzene. Crystals precipitated upon standing; they were filtered and washed with benzene, ether, and water. O-Benzoylphenylalanyl-N-benzoylserine was recrystallized from a mixture of dichloroethane and alcohol. M.p. 171°. Yield 2.0 g. The substance was soluble in alcohol, acetone, hot dichloroethane and insoluble in water, benzene, and toluene.

The compound has not been reported in the literature.

Found %: C 67.23, 67.47; H 5.38, 5.31; N 6.09, 5.98. $C_{26}H_{24}O_6N_2$. Calculated %: C 67.82; H 5.22; N 6.08.

Preparation of the Isopropyl Ester of N,O-Di(phthalylglycyl)-serine (V)

1.38 g of serine isopropyl ester hydrochloride and 3.6 g of phthalylglycyl acid chloride were heated to 100-105° (glycerine bath) in 10 ml of dioxane until the evolution of hydrogen chloride ceased, and for 10 minutes more. The dioxane was distilled off in vacuum. The residue, a dark, tarry mass, was dissolved with heating in 6 ml of dioxane. 8 ml of ligroin was added to the solution. After strong shaking, crystallization started. 10 ml more of ligroin was added to the solution, the residue was filtered, washed with petroleum ether, and recrystallized from a mixture of alcohol and dioxane (1:1). 2.7 g of the isopropyl ester of N,O-di-(phthalylglycyl)serine was obtained. Yield 69% of the theoretical. M.p. 170-171°. The substance crystallized in the form of very thin needles; it was soluble in dioxane and dichloroethane, difficultly soluble in alcohol, and insoluble in water and ligroin.

The compound has not been reported in the literature.

Found %: C 59.67, 59.48; H 4.70, 4.64; N 8.15, 8.20. $C_{36}H_{35}O_9N_2$. Calculated %: C 59.88, H 4.41; N 8.06.

Preparation of the Methylamide of O-(benzoylphenylalanyl)-N-benzoylserine (VI)

a) Preparation of the methylamide of N-benzoylserine. 5g of N-benzoylserine was esterified with methyl alcohol under the usual conditions for the esterification of amino acids and their derivatives. The oil remaining after the removal of the methyl alcohol and hydrogen chloride was treated with an ether solution of methylamine, and allowed to stand for two days. The ether was removed in vacuum, and the residual oil crystallized upon standing. After recrystallization from absolute alcohol, the methylamide of N-benzoylserine was obtained in the form of long, white needles, readily soluble in water, aqueous alcohol, with heating in dioxane, absolute alcohol, and methyl ethyl ketone. M.p. 146.5°. Yield 3.5 g, 65 % of the theoretical.

The compound has not been reported in the literature.

Found %: C 59.60, 59.70; H 6.35, 6.45; N 12.55, 12.68. $C_{22}H_{24}O_3N_2$. Calculated %: C 59.45; H 6.30; N 12.61.

b) Preparation of the methylamide of O-(benzoylphenylalanyl)-N-benzoylserine. 0.5 g of the methylamide of N-benzoylserine, dissolved in dioxane, was added to a chloroform solution of benzoylphenylalanyl acid chloride obtained

from 1 g of benzoylphenylalanine. The mixture was heated for 4 hours at 50-60° and allowed to stand overnight. The oil remaining after the removal of the solvents was treated with absolute benzene. Upon standing, crystals formed, which were washed many times with benzene, sodium carbonate solution, and water. The substance was recrystallized from alcohol and dried in vacuum at 80° over phosphoric anhydride. M.p. 181°. Yield 0.8 g. 77% of the theoretical.

The compound has not been reported in the literature.

Found %: C 67.93, 67.87; H 5.98, 5.85; N 8.62, 8.78. $C_{27}H_{27}O_3N_3$. Calculated %: C 68.49; H 5.71; N 8.88.

SUMMARY

Methods for the synthesis of O,N-peptides of serine were studied. The following peptides were prepared: O-(benzoylphenylalanyl)-N-benzoylserine, the ethyl ester of O-(benzoylaminoisobutyryl)-N-benzoylserine, the isopropyl ester of N,O-di-(phthalylglycyl)serine, and the methylamide of O-(benzoylphenylalanyl)-N-benzoylserine.

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Received January 11, 1953

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* See Consultants Bureau English translation, page 1675.

** See Consultants Bureau English translation, page 1101.



REACTION OF HYDROGEN SULFIDE WITH OXIDES OF THE ACETYLENIC AND VINYLACETYLENIC SERIES

I. SYNTHESIS OF VINYL AND ALKYL THIOPHENES

F. Ya. Perveev and N. I. Kudryashova

By the reaction of hydrogen sulfide with ethylene oxides, hydroxyethylmercaptans or dithioglycols are formed in relation to the temperature conditions and the ratio of the reagents [1]. Thioglycerines are obtained from glycidic oxides and hydrogen sulfide in the form of two isomers [2]. By passing a mixture of hydrogen sulfide and ethylene oxide over Al_2O_3 at 350-400°, thiophene, 2,5-dimethylthiophene, and other higher homologs of thiophene, as well as the lower mercaptans are formed [3]; at 200-250°, thioxane and dithiane [4].

The reaction of hydrogen sulfide with the following oxides, whose formulas and constants are given in the Table, was studied: 2-methylepoxy-1,2-hexen-5-yne-3 (I), 3-methylepoxy-2,3-hepten-6-yne-4 (II), 2-ethylepoxy-1,2-pentyne-3 (III), and 3-methylepoxy-2,3-hexyne-4 (IV).

A colorless, readily volatile liquid with a specific odor was obtained by the reaction of oxide (I) with hydrogen sulfide. An acid of composition $C_8H_6O_2S$, melting at 120-121° (8'-methyl- α -thiophene carboxylic acid) was obtained by the oxidation of this substance and its hydrogenation product with potassium permanganate. The structure α -vinyl-8'-methylthiophene could be assigned to the product synthesized on the basis of the data obtained. The fact that the constants of the substance obtained coincided with those of the compound synthesized by another method [5] served as a confirmation of the above conclusion.

No.	Formula	Melting point	d_4^{20}	n_D^{20}
(I)	$CH_2=CH-C\equiv C-\underset{\text{O}}{\text{C(CH}_3\text{)-CH}_2}$	50-51° (15 mm)	0.9249	n_D^{20} 1.4739
(II)	$CH_2=CH-C\equiv C-\underset{\text{O}}{\text{C(CH}_3\text{)-CH-CH}_3}$	54-55° (12 mm)	0.9005	1.4881
(III)	$CH_3-C\equiv C-\underset{\text{O}}{\text{C(C}_2\text{H}_5\text{)-CH}_2}$	40-41° (8 mm)	0.8966	1.4436
(IV)	$CH_3-C\equiv C-\underset{\text{O}}{\text{C(CH}_3\text{)-CH-CH}_3}$	59-60° (28 mm)	0.8856	1.4410

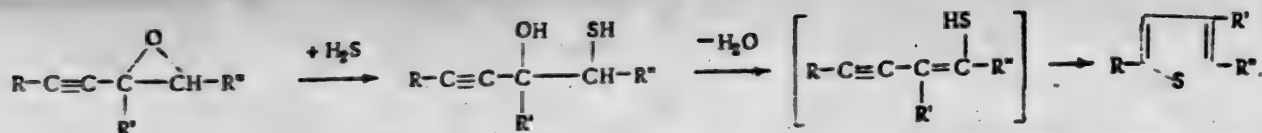
α -Vinyl- α' ,8'-dimethylthiophene was obtained by the action of hydrogen sulfide on oxide (II), and α -methyl-8'-ethylthiophene, from oxide (III). The physical constants of α -methyl-8'-ethylthiophene, previously reported in the literature [6] coincide with those of the substance

obtained. α , α' ,8'-Trimethylthiophene is formed by the reaction of hydrogen sulfide with oxide (IV). It is an easily volatile colorless liquid with a specific odor which is soluble in strong sulfuric acid, gives a characteristic indophenone color with isatin sulfate, and forms a white crystalline precipitate with mercury acetate.

Based on the above results, it can be considered established that the reaction of hydrogen sulfide with oxides of the acetylenic and vinylacetylenic series is a general one for the synthesis of vinyl and alkylthiophenes.

Up to now alkyl thiophenes have been prepared by the treatment with phosphorous pentasulfide of γ -keto acids [7], γ -dicarboxylic acids [8], 1,4 diketones [9], or from furane derivatives by the action of hydrogen sulfide at high temperatures in the presence of a catalyst [10], and others. Vinyl thiophenes were prepared by the reduction of acetylthiophenes to the corresponding alcohols and their subsequent dehydration [11, 12, 13] and by the reaction of thienyl magnesium bromide with vinyl chloride in the presence of $CoCl_2$ [14].

The formation of vinyl and alkylthiophene from oxides of the acetylenic and vinylacetylenic series by the reaction with hydrogen sulfide, evidently, occurs according to the following scheme:



The rate of formation of the thiophene derivatives depends on the temperature conditions of the reaction, and the structural peculiarities of the oxides. Disubstituted oxides of type (III) react with hydrogen sulfide considerably more rapidly than the trisubstituted of type (IV). In addition, radicals which substitute for the acetylenic hydrogen have a considerable effect on the reactivity of the oxide ring. Thus, for example, 2-methylepoxy-1,2-hexen-5-yne-3 (I) reacts with hydrogen sulfide at room temperature with a great evolution of heat, while heating for several hours is necessary for the preparation of α -vinyl- α' , β' -dimethylthiophene from 3-methylepoxy-2,3-hepten-6-yne-4 (II).

EXPERIMENTAL

1. Preparation of α -Vinyl- β' -methylthiophene

20 g of $\text{Ba}(\text{OH})_2$ and 150 ml of water were placed into a round bottomed flask with a mechanical stirrer, and a stream of hydrogen sulfide was passed in with intensive stirring with a simultaneous addition of 30 g of oxide (I). The addition of the oxide was regulated in such a manner that the temperature of the reaction mixture did not go above 50° . After the addition of the oxide, the hydrogen sulfide was passed in for one hour more. The reaction mixture was then acidified with the calculated amount of acetic acid. The reaction products were extracted with ether, the ether layer was dried, the ether was removed, and after 2 distillations, the substance was obtained in the form of a colorless liquid with b.p. $67-70^\circ$ at 10 mm, n_D^{20} 1.5580, d_4^{20} 1.0110. It gradually polymerized upon storage in the air to form a viscous mass. Yield 25 g, 73-75% of the theoretical. It dissolved in strong sulfuric acid, gave a characteristic indophenone reaction with isatin. It formed a crystalline precipitate with mercury acetate.

0.4539 g substance: 0.8470 g BaSO_4 . Found %: S 25.63. $\text{C}_7\text{H}_8\text{S}$. Calculated %: S 25.80.

Hydrogenation of α -vinyl- β' -methylthiophene. The hydrogenation was effected over Raney Ni in ether solution. 1158 ml of hydrogen (22° , 764 mm) was consumed for the hydrogenation of 6 g of the substance; 1085 ml of H_2 was required based on one double bond. The hydrogenation product was first dried with CaCl_2 and then with metallic sodium, and it was distilled over Na, b.p. $158-159^\circ$, n_D^{20} 1.5061, d_4^{20} 0.9652.

Oxidation of α -vinyl- β' -methylthiophene. 22.4 g of KMnO_4 was used for the oxidation of 6.28 g of the substance. The oxidation was conducted in alkaline medium (3 g of NaOH in 800 ml of water). No neutral substances and volatile acids with the exception of an acid of the composition $\text{C}_6\text{H}_6\text{O}_2\text{S}$, which was extracted with ether from the acidified aqueous solutions, could be detected among the oxidation products. The ether was removed and the substance obtained was recrystallized from water; m.p. $120-121^\circ$.

0.3208 g substance: 0.5236 g BaSO_4 . Found %: S 22.41. $\text{C}_6\text{H}_6\text{O}_2\text{S}$. Calculated %: S 22.55.

Oxidation of the hydrogenation product of α -vinyl- β' -methylthiophene. 24.4 g of KMnO_4 was used for the oxidation of 4.7 g of the substance. The oxidation was conducted in alkaline medium. An acid was isolated from among the products, which melted at $120-121^\circ$ and did not give a depression in melting point when mixed with the previously isolated product.

2. Preparation of α -Vinyl- α' , β' -dimethylthiophene.

30 g of 3-methylepoxy-2,3-hepten-6-yne-4 (II), 20 g of $\text{Ba}(\text{OH})_2$ and 150 ml of water were used. The hydrogen sulfide was passed into the reaction mixture for 8 hours at $60-70^\circ$.

17 g of a substance with b.p. $68-70^\circ$ at 8 mm was isolated; n_D^{20} 1.5545, d_4^{20} 0.9938; MR_D 44.6. $\text{C}_8\text{H}_{10}\text{S}$. Calculated 43.47.

The substance obtained was a colorless, mobile liquid, with a characteristic odor. Upon storage in the air, it yellowed. It formed a white precipitate with mercury acetate which decomposed at 250° . It gave a dark wine-red coloration with isatin and strong sulfuric acid. Yield 50% of the theoretical.

0.3846 g substance: 0.6438 g BaSO_4 . Found %: S 22.99. $\text{C}_8\text{H}_{10}\text{S}$. Calculated %: S 23.20.

If the synthesis was effected at $80-90^\circ$, the reaction was completed in 2 hours, and the yield of the product was somewhat increased. In the first, as well as in the second synthesis, the formation of tarry products occurred, evidently, because of the polymerization of the oxide.

3. Preparation of α -methyl- β '-ethylthiophene

2-Ethyl-1-chloropentyne-3-ol-2. 36 liters of methylacetylene was passed in over a 12-hour period into an ether solution of 1 mole of ethyl magnesium bromide. Then 15 g of 1-chlorobutanone-2 was added with stirring and cooling (water and ice). The reaction mixture was left to stand overnight. The organo-magnesium complex was decomposed with 30% acetic acid. The ether layer was separated, the water was extracted with ether, dried with Na_2SO_4 , and the ether was removed. The substance obtained had the following constants after 2 distillations: b.p. 75-77° at 8 mm, n_D^{20} 1.4711, d_4^{20} 1.0571; MR_D 38.8. $\text{C}_7\text{H}_{11}\text{OClF}$. Calculated 38.92.

0.2483 g substance: 0.2436 g AgCl. 0.1135 g substance: 18.7 ml CH_4 (16.5°, 767.4 mm). Found %: Cl 24.27; Active H 0.695. $\text{C}_7\text{H}_{11}\text{OCl}$. Calculated %: Cl 24.18; active H 0.688.

2-Ethylepoxy-1,2-pentyne-3 (III). Oxide (III) was isolated upon the treatment of the chlorohydrin with powdered KOH in ether solution and was a colorless liquid with b.p. 40-41° at 8 mm, n_D^{20} 1.4436, d_4^{20} 0.8966; MR_D 32.9. $\text{C}_7\text{H}_{10}\text{OF}$. Calculated 32.8.

0.1164, 0.1282 g substance: 0.3248, 0.3574 g CO_2 ; 0.0969, 0.1055 g H_2O . Found %: C 76.15, 76.08; H 9.32, 9.21. $\text{C}_7\text{H}_{10}\text{O}$. Calculated %: C 76.32; H 9.15.

α -Methyl- β '-ethylthiophene. 100 ml of water, 15 g of $\text{Ba}(\text{OH})_2$, and 25 g of oxide (III) were placed in a round-bottomed flask with a mechanical stirrer and a reflux condenser. Hydrogen sulfide was passed in for 15 hours at 50-60°. The processing of the reaction mixture was effected by the above reported method. The product obtained was dried with MgSO_4 and vacuum distilled at 50-51° (10 mm); 15 g of methylethylthiophene was isolated and 4 g of the oxide (III) was recovered. Methylethylthiophene was dried and distilled over metallic sodium at 161-162°; d_4^{20} 0.9710, n_D^{20} 1.5070; MR_D 38.69. $\text{C}_7\text{H}_{10}\text{SF}_2$. Calculated 39.31.

The substance dissolved in sulfuric acid and gave a characteristic violet coloration with isatin sulfate and formed a crystalline compound with mercury acetate.

0.1984, 0.1715 g substance: 0.3648, 0.3146 g BaSO_4 . Found %: S 25.25, 25.19. $\text{C}_7\text{H}_{10}\text{S}$. Calculated %: S 25.41.

Oxidation of methylethylthiophene. 3 g of the substance, 15.5 g of KMnO_4 (calculated for the oxidation of the ethyl group) 1.5 g of NaOH, and 500 ml of water were used. The KMnO_4 was added gradually in small portions, the oxidation was continued for 8 hours at ordinary temperatures. Neutral products were not detected. An acid with m.p. 97-99° was isolated by extraction of the acidified aqueous solution.

4. Preparation of α, α', β' -Trimethylthiophene

3-Methyl-2-chlorohexyne-4-ol-3. The chlorohydrin was prepared by the above method. 80 g of 2-chlorobutanone-3 was used for 1 mole of methylacetylenyl magnesium bromide. 72 g of the substance (65% of theory) with b.p. 66-67.5° at 7 mm, n_D^{15} 1.4671, d_4^{15} 1.0535, MR_D 38.62. $\text{C}_7\text{H}_{11}\text{OClF}$. Calculated 38.92.

0.2817 g substance: 0.2745 g AgCl. Found %: Cl 24.10. $\text{C}_7\text{H}_{11}\text{OCl}$. Calculated %: Cl 24.18.

3-Methylepoxy-2,3-hexyne-4 (IV). A substance with b.p. 43-44° at 12 mm was isolated by the treatment of the chlorohydrin with powdered KOH in ether solution; MR_D 32.84. $\text{C}_7\text{H}_{10}\text{OF}$. Calculated 32.80.

0.1239, 0.1200 g substance: 0.3468, 0.3350 g CO_2 ; 0.1029, 0.1003 g H_2O . Found %: C 76.27, 76.18; H 9.29, 9.35. $\text{C}_7\text{H}_{10}\text{O}$. Calculated %: C 76.32; H 9.15.

α, α', β' -Trimethylthiophene. 100 ml of water, 15 g of $\text{Ba}(\text{OH})_2$, 20 g of oxide (IV) were placed into a round bottomed flask with a mechanical stirrer. Hydrogen sulfide was passed in at a reaction mixture temperature of 50-60° for 10 hours. After the corresponding processing of the reaction mixture, the synthesized substance was distilled over metallic sodium. 8 g was isolated with b.p. 162-163°. n_D^{20} 1.5104, d_4^{20} 0.9730; MR_D 38.82. $\text{C}_7\text{H}_{10}\text{SF}_2$. Calculated 39.31.

0.2125, 0.1988 g substance: 38.5 ml NaOH ($T = 0.003747$); 38.0 ml NaOH ($T = 0.003275$). Found %: S 25.4, 25.1. $\text{C}_7\text{H}_{10}\text{S}$. Calculated %: S 25.41.

In addition to trimethylthiophene, 10 g of the starting oxide was isolated during the distillation of the product obtained. The yield of trimethylthiophene was 73% of the theoretical based on the reacted oxide. At 80-90° the reaction proceeded to completion and is completed within a shorter time.

SUMMARY

1. A general method was developed for the preparation of vinyl and alkylthiophenes by the reaction of

oxides of the acetylenic and vinylacetylenic series with hydrogen sulfide in the presence of $\text{Ba}(\text{OH})_2$.

2. α -Vinyl- β '-methylthiophene, α -vinyl- α' , β' -dimethylthiophene, α -methyl- β' -ethylthiophene, and α , α' , β' -trimethylthiophene were synthesized with this method.

3. A probable scheme for the formation of vinyl and alkylthiophenes was proposed.

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Received January 6, 1953.

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SYNTHESIS BASED ON ANABASINE

VI. AMINATION OF ANABASINE, N-METHYLANABASINE, AND NICOTINE

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The previous investigation [1] was concerned with the study of the transformation products of N-(8-hydroxyethyl)anabasine. The present communication reports the results of the study of the amination reaction of anabasine, N-methylanabasine, and nicotine without solvents. The amination of anabasine and its derivatives with alkali metal amides in various solvents [2, 3, 4] showed that better yields of the reaction products were obtained by using dimethylaniline. In view of the fact that dialkyl amines are not always readily available solvents, and that A. Chichibabin [5] showed with pyridine that amination can occur by the direct reaction of the reagents, it was of interest to conduct this reaction with anabasine, N-methylanabasine, and nicotine. The main subject of this study of the amination reaction was anabasine.

The starting substances were prepared in the following manner: anabasine was separated from a low boiling fraction of anabasine sulfate by the hydrochloride method [6]. N-methylanabasine was prepared by reacting anabasine with formaldehyde and formic acid by the method of Orekhov and Norkina [7]. Nicotine was separated from nicotine sulfate by the usual method. The bases obtained were characterized by physical constants and by the preparation of characteristic salts. A ratio of base to sodium amide of 1 mole to 2 moles with a small excess of the latter. The amination of anabasine was effected by heating a mixture of the reacting substances under the usual conditions and under pressure for 12 hours at various temperatures.

α' -Aminoanabasine could be obtained in a yield of 22.2% by effecting the reaction under pressure (in an autoclave) at 150-160°. Further increasing the temperature leads to a strong tarring of the reaction products. The amination of anabasine under the usual conditions (without an autoclave) also gave α' -aminoanabasine with a yield of 6.80%. In both cases, noticeable amounts of α -aminoanabasine could not be isolated, which were always formed during the amination of anabasine in a solvent (see the Table). Increasing the reaction time, did not effect the yield of the products of the amination to any great extent under ordinary conditions, as well as under pressure.

Expt. No.	Reagents (in g)		Heating temperature	Yield of aminocanabasine	
	Anabasine	Sodium amide		(in g)	(in % of theoretical)
1	10.0	5.76	100°	—	—
2	20.0	11.50	130 - 140	0.56	2.57
3	13.4	8.62	140 - 150	1.40	9.58
4	20.0	11.50	150 - 160	4.85	22.2
5	15.5	8.78	160 - 180	1.16	6.84
6	20.0	11.50	180 - 200	1.39	6.43

The amination of nicotine was effected at 150-160° (in an autoclave) as with anabasine, and α' -aminonicotine was obtained in a yield of 87.9%. It must be mentioned that the yield of α' -aminonicotine considerably exceeded that total yield of aminonicotines obtained by the amination of nicotine in xylene as a solvent [8].

The amination of N-methylanabasine was effected by heating a mixture of the reacting substances at 140-155° for 12 hours. In contrast to anabasine and nicotine, two isomers were obtained as a result of the reaction: α -

amino-N-methylanabasine in a yield of 23.3% and α' -amino-N-methylanabasine in a yield of 37.7%. The total yield of the N-methylaminocanabasines, 61.0%, does not differ from the total yield of the products of the amination in dimethylaniline [9]. The reaction, effected under the above conditions but under pressure made it possible to obtain a total yield of aminoderivatives of 70.6%.

Therefore, considerably better results were obtained by the amination of nicotine and N-methylanabasine with sodium amide in an autoclave in comparison to those obtained by effecting the reaction in solvents (without an autoclave). This can be explained by the presence of a methyl group on the nitrogen of these bases which increases the activity of the α and α' hydrogen atoms in the pyridine nucleus, especially the α' -hydrogen atom, since considerably more of α' -aminoderivative is obtained. On the other hand, nicotine and N-methylanabasine are less prone to tarring than anabasine.

EXPERIMENTAL

1. Separation of anabasine from a mixture of anabasine and lupinine. 390 g of a mixture of anabasine and lupinine (containing 88.4% of anabasine) was dissolved in 1000 ml of acetone. 77.5 g of hydrogen chloride in acetone was added in small portions with cooling and stirring to the solution. The precipitation of anabasine hydrochloride started. The reaction mass was allowed to stand until the following day. The precipitate was filtered, washed many times with acetone, and recrystallized from a mixture of alcohol and acetone. For the preparation of the base, the hydrochloride was dissolved in a small volume of water and treated with a 40% solution of potassium hydroxide until a weakly basic reaction occurred. The oil which precipitated was extracted with benzene. The benzene solution was dried over fused sodium sulfate and the solvent removed. The residue was vacuum distilled at 139-142° (14 mm). Yield 313.7 g (91% of the theoretical).

2. Amination of anabasine (in an autoclave) (typical experiment). A mixture of 20 g of anabasine (1 mole) and 11.5 g of sodium amide (2.4 moles) was heated in an autoclave for 12 hours at 150-160°. The reaction product which was a solid dark mass, was decomposed (with cooling) with a small amount of water. The solution obtained was saturated with sodium carbonate and extracted many times with ether. The ether extracts were combined and dried with fused potassium carbonate. After the removal of the solvent, the residue was vacuum distilled.

The following fractions were obtained: Fraction 1: 137-139° (10 mm), 3.46 g, unchanged anabasine; fraction 2: 165-190° (10 mm) 4.85 g (yield 22.2 %), α '-aminoanabasine.

The second fraction was dissolved in hot toluene. Upon standing, crystalline α '-aminoanabasine precipitated from the solution. Recrystallized from toluene, α '-aminoanabasine had an m.p. of 109°. α '-Aminoanabasine was readily soluble in water and alcohol, difficultly in ether, and benzene. The picrate had an m.p. of 231-233°. A mixed melting point determination with α '-aminoanabasine picrate prepared by the amination of anabasine in dimethylaniline did not give a depression.

3. Amination of anabasine. 20 g of anabasine (1 mole) and 11.5 g of sodium amide (2.4 moles) were heated for 12 hours. The subsequent processing was as in the previous experiment. The residue was vacuum distilled, and the following fractions were obtained: fraction 1, 135-140° (10 mm), 6.5 g, unchanged anabasine; fraction 2, 165-180° (10 mm), 1.48 g (6.8%), α '-aminoanabasine.

Crystalline α '-aminoanabasine was obtained by solution in toluene. After recrystallization from hot toluene, the m.p. was 108-109°. α '-Aminoanabasine picrate had an m.p. of 231-233°.

4. Amination of nicotine. A mixture of 30 g of nicotine (1 mole) and 17.28 g (2.4 moles) of sodium amide was heated in an autoclave for 12 hours at 150-160°. The reaction product was processed in the usual manner. After distillation in vacuum, a fraction boiling at 164-170° (0.5 mm), 28.6 g (87.7%) was obtained. The constants corresponded with the literature data for α 'aminonicotine [9].

The hydrochloride. Concentrated hydrochloric acid was added dropwise to the α '-aminonicotine until an acid reaction appeared on Congo. The solution obtained was evaporated to dryness on the water bath. The crystalline residue had an m.p. 136-138° after two recrystallizations from alcohol.

5. Amination of N-methylanabasine. 30 g (1 mole) of N-methylanabasine and 16.6 g (2.4 moles) of sodium amide were heated in an autoclave at 150-160° for 12 hours. The reaction mixture was decomposed with water, saturated with sodium carbonate, and exhaustively extracted with ether. The combined ether extracts were dried over fused potassium carbonate. The residue, after the removal of the solvent, was vacuum distilled. The following fractions were obtained: fraction 1: 155-160° (7 mm), 7.6 g (yield 23.3%), α -amino-N-methylanabasine; fraction 2: 162-167° (7 mm), 12.3 g (yield 37.7%), α '-amino-N-methylanabasine. α -Amino-N-methylanabasine picrate (from alcohol) had an m.p. 234-235°. α '-Amino-N-methylanabasine picrate (from water) had an m.p. 216-217°.

6. Amination of N-methylanabasine. A mixture of 30 g (1 mole), of N-methylanabasine and 21.5 g (2.9 moles) of sodium amide were heated in an autoclave at 150-160° for 12 hours. The cooled mass was decomposed with water and extracted with benzene. The benzene solution was dried over fused potassium carbonate; the solvent was removed, and the residue subjected to vacuum distillation (at 13 mm).

Fraction 1: b.p. 155-160° (7 mm), α -amino-N-methylanabasine, 8 g (yield 24.5%); fraction 2: 162-167° (7 mm), α '-amino-N-methylanabasine, 15.0 g (yield 46.1%). α -Amino-N-methylanabasine picrate melted at 233-235°. α '-Amino-N-methylanabasine picrate melts at 216-219.

SUMMARY

1. It was shown that the amination reaction of anabasine, nicotine, and N-methylanabasine with sodium amide can occur without solvents; the α' -isomer was obtained preferentially by the amination of anabasine and nicotine. Upon the amination of N-methylanabasine, a mixture of two isomeric amino-N-methylanabasine was obtained with the α' -isomer predominating.

2. The total yield of the amination products of anabasine, N-methylanabasine, and nicotine in an autoclave without a solvent was greater than when the reaction was conducted in dialkylamine solutions.

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Received September 8, 1952.

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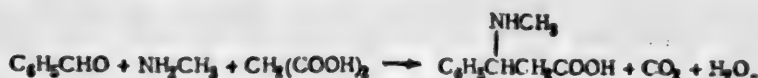


SYNTHESIS OF β -PHENYL- β -(N-METHYLAMINO)PROPIONIC ACID AND SEVERAL OF ITS DERIVATIVES

V. M. Rodionov and E. V. Yavorskaya

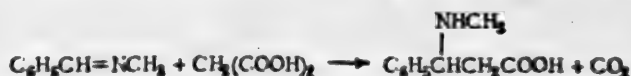
The problem of the present investigation was the preparation of N -alkyl- β -amino acids in order to compare their properties and transformations with β -amino acids with primary amino groups. β -Phenyl- β -(N -methylamino)propionic acid was prepared initially.

This compound was first synthesized by Rodionov and Zenkovich by the reaction between benzaldehyde, malonic acid, and an alcoholic methylamine solution.



The main product in addition to the methylamino acid was cinnamic acid.

Somewhat later phenylmethylaminopropionic acid was obtained by Johnson [1] in greater yield, who synthesized this compound by condensation of benzalmethylamine with malonic acid in an absolute alcoholic medium.

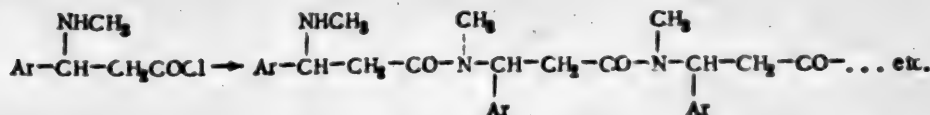


The yield of the N -methylamino acid by this method was 40% of the theoretical based on the benzal derivative. Cinnamic acid was also formed. Yield, 38% of the theoretical.

It was shown by the authors that, if the condensation of benzalmethylamine with malonic acid was effected in a benzene medium, an increase of the yield of the methylamino acid to 50-55% and a decrease in the formation of cinnamic acid to 27-33% occurred.

It was decided to prepare as the initial derivative of N -methyl- β -phenyl- β -alanine, N -methylphenylglyoxal-dione by the Hoffman reaction. N -methyl- β -phenyl- β -alanyl chloride, necessary for the preparation of the amide, was prepared by the action of thionyl chloride on N -methyl- β -phenyl- β -alanine and was isolated as the hydrochloride in a good yield.

A series of difficulties were encountered during the preparation of N -methyl- β -phenyl- β -alanyl amide. During attempts to amidate the acid chloride with dry ammonia, the formation of high molecular compounds occurred arising, evidently, as a result of the intermolecular condensation of the acid chloride with an N -methyl group of a second molecule.



The preparation of the ester of the amino acid was accompanied by deamination; a mixture of the esters of cinnamic and β -phenyl- β -(N -methylamino)propionic acids resulted. As a result, the ester of the amino acid was isolated in the form of the hydrochloride and in low yield. In subsequent experiments, the reaction for the preparation of the amide was conducted without the isolation of the ester in the free state by the action of ammonia in the cold on a solution of the acid chloride in alcohol. The reaction mixture obtained was usually allowed to stand for 10-12 days at room temperature, and the desired amide was isolated in a yield of 25-30% of the theoretical.

The ease of the process of deamination of the amide of N -methyl- β -phenyl- β -alanine, as well as the possible

action of hypobromite on the unprotected secondary amino group complicated the course of the Hoffmann reaction, and for this reason, N-methylphenylglyoxalidone was only prepared in a low yield (20-25%). Tests conducted at the Microbiological Institute of the Academy of Sciences of the U.S.S.R. showed that the glyoxalidone did not possess antibiotic activity.

For the further characterization of β -phenyl- β -(N-methylamino)propionic acid, its N-nitroso-N-benzoyl derivative and its amide were synthesized in good yields.

During attempts to cyclize N-benzoyl-N-methyl- β -phenyl- β -alanylamide into 1-methyl-2,6-diphenyl-4-oxo-tetrahydropyrimidine by the action of acetic anhydride, a thick oil was isolated which did not distill at ordinary or reduced pressures. The reaction product did not lend itself for purification by means of crystallization from various organic solvents either. N-benzoyl-N-methyl- β -phenyl- β -alanine was isolated in unchanged form from the mother liquor without contamination with benzoic acid. The absence of the last compound showed that reaction of N-benzoyl-N-methyl- β -phenyl- β -alanylamide with acetic anhydride was not accompanied by trans-acylation, in contrast to amino acids with primary amino groups [2].

The dehydration of the amide did not occur even upon heating with oxalic acid in benzene and toluene. Upon heating N-benzoyl-N-methyl- β -phenyl- β -alanylamide with oxalic acid without solvents, the reaction started at 145-150°. It was shown that the main product of the reaction was cinnamic amide which formed as a result of the deamination process of the amide, and that the formation of the tetrahydropyrimidine ring did not occur.

EXPERIMENTAL

Synthesis of N-methyl- β -phenyl- β -alanine. A mixture of 28.5 g of benzaldehyde, 23 g of malonic acid, and 115 ml of benzene was heated to boiling on the water bath for 8 hours. The evolution of carbon dioxide gas and the formation of a precipitate of the amino acid occurred. At the end of the reaction, ether was added to the cooled reaction mixture for the complete precipitation of the amino acid (the ether and benzene used in this experiment were dried over calcium chloride).

The precipitated amino acid was filtered, washed with ether on the funnel, and dried. M.p. 167-168°, yield 20.8 g, i.e., 52.5% of the theoretical. 11.2 g of the cinnamic acid was isolated from the ether benzene filtrate which was 34.2% of the theoretical.

Preparation of β -phenyl- β -(N-methylamino)propionylacid chloride. 10 g N-methyl- β -phenyl- β -alanine was added gradually to 22 g of thionyl chloride with ice cooling. The mixture obtained was heated on the water bath for 2 hours at 45-50° (thermometer inside the flask). The precipitated light yellow residue which was the hydrochloride of N-methyl- β -phenyl- β -alanine, was filtered, washed with benzene, then ether, and dried in a vacuum desiccator. Yield 11.2 g of white crystals, (about 85.7 % of the theoretical). The substance melted at 128-129° (with decomposition).

Found %: Cl 30.10, 29.92; N 6.12. $C_{10}H_{13}ONCl_2$. Calculated %: Cl 30.34; N 5.98.

Synthesis of the ester of N-methyl- β -phenyl- β -alanine. 2 g of N-methyl- β -phenyl- β -alanine, 10 ml of absolute alcohol, and 2 g of concentrated sulfuric acid were heated to boiling on a water bath for 5 hours. At the end of the reaction, the alcohol was removed, and the solution was extracted with ether after neutralization with sodium hydroxide. The oil remaining after the removal of the ether did not give a definite boiling point at ordinary, as well as reduced pressures. The odor of methylamine was detected upon distillation. Evidently, the process of deamination occurred, and the ether ester of N-methyl- β -phenyl- β -alanine was partially converted into ethyl cinnamate. This assumption was proved by the analysis for nitrogen of the mixture of esters. The nitrogen content was equal to 3.7 and 3.9 %, whereas the ethyl ester of N-methyl- β -phenyl- β -alanine should contain 6.76% of nitrogen. The ester of the amino acid was isolated in the form of the hydrochloride by passing hydrogen chloride into an ether solution of the mixture of esters. White crystals with m.p. 113-114°.

Found %: N 5.91, 6.12. $C_{10}H_{17}O_2N \cdot HCl$. Calculated %: N 5.75.

Synthesis of N-methyl- β -phenyl- β -alanylamide. 10 g of N-methyl- β -phenyl- β -alanylacid chloride hydrochloride was dissolved in 100 ml of absolute alcohol, saturated with ammonia in the cold, and left in a closed container for 8-10 days at room temperature. The precipitated ammonium chloride was filtered, and the alcohol was removed. The residue after the removal of the alcohol was a mixture of crystals, soluble in a sufficient amount of water, and an oil insoluble in water and hydrochloric acid. After treating the residue with water, the oil which separated was extracted with ether, and after the removal of the ether and rectification, 4 g of ethyl cinnamate was obtained.

The remaining aqueous solution was evaporated to a small volume. The separated crystals of N-methyl- β -phenyl- β -alanylamine hydrochloride were recrystallized from ethyl alcohol. 2.5 g white needles with m.p. 215-216° was obtained. The yield of the amide hydrochloride was 26.7 %, and about 58% of the theoretical based on the acid chloride not subjected to the deamination process.

Found %: N 13.24, 13.27. $C_{10}H_{13}ON_2Cl$. Calculated %: N 13.05.

The base of N-methyl- β -phenyl- β -alanylamine was very soluble in H_2O . In order to isolate it, an aqueous solution of the hydrochloride was neutralized with sodium carbonate, evaporated to dryness, and extracted with absolute alcohol. After the removal of the alcohol, the compound obtained was recrystallized from benzene. White crystals with m.p. 103-104°.

Found %: N 15.75, 15.76. $C_{10}H_{14}ON_2$. Calculated %: N 15.72.

Synthesis of N-methylphenylglyoxalidone. 2 g of bromine was added dropwise to a solution of 4 g of potassium hydroxide in 20 ml of water cooled to -8-10°. 1.6 g of N-methyl- β -phenyl- β -alanylamine hydrochloride was added gradually to the obtained solution of the hypobromite at the same temperature. After 2 hours, the clear yellow solution obtained was slowly heated to 80°. At about 55°, the liquid in the flask clouded as a result of the separation of the intermediate compound in the form of an oil. Upon further increase in temperature, the liquid once more became transparent. The heating was continued for 10 minutes at 80°. Upon cooling, yellow crystals of N-methylphenylglyoxalidone slowly precipitated from the solution in an 0.3 g quantity (22.9% of the theoretical). Its melting point was 147-148°, and after recrystallization from water with carbon or from alcohol, white needles with m.p. 150-151° were obtained.

Found %: C 67.98, 68.08; H 6.74, 6.82; N 16.14. $C_{10}H_{12}ON_2$. Calculated %: C 68.16; H 6.81; N 15.90.

Synthesis of N-nitroso-N-methyl- β -phenyl- β -alanine. A solution of 2 g of sodium nitrite in 20 ml of water was added to a solution of 4 g of the N-methylamino acid in 40 ml of 5% hydrochloric acid. The reaction proceeded at room temperature at first and then at 30-35°. A precipitate of the nitroso compound formed gradually in the form of white crystals with m.p. 104-106°. After recrystallization from water, platelets melting at 107-108° were obtained. Yield of the recrystallized compound, 3.8 g (about 81.7% of the theoretical).

Found %: N 13.58, 13.36. $C_{10}H_{12}O_3N_2$. Calculated %: N 13.46.

Benzoylation of N-methyl- β -phenyl- β -alanine. 25 g of N-methyl- β -phenyl- β -alanine and 95 g of potassium hydroxide were dissolved in 250 ml of water, and 25 g of benzoyl chloride was added to the solution at room temperature. The reaction was conducted with mechanical stirring for 2 hours. The clear solution was then acidified with hydrochloric acid to Congo. The precipitated mixture of the benzoyl derivative and benzoic acid was treated with boiling water. After cooling the hot solution, 5 g of benzoic acid with m.p. 110-115° precipitated from it. The undissolved residue, 29 g of benzoylmethylamino acid with m.p. 156-157°, was recrystallized from alcohol and melted at 157-158°. Yield of the benzoyl derivative was 74.5 % of the theoretical.

Found %: N 5.24, 5.30. $C_{17}H_{17}O_3N$. Calculated %: N 4.95.

Preparation of N-benzoyl-N-methyl- β -phenyl- β -alanylamine.

1) From N-methyl- β -phenyl- β -alanine. 1 g N-methyl- β -phenyl- β -alanine and 1 g of thionyl chloride were heated for 2 hours at 40-45°. The excess thionyl chloride was removed in vacuum. The obtained dark yellow oil was dissolved in dry benzene and treated with ammonia in the cold. The precipitated yellow residue was washed with benzene, water, and recrystallized from alcohol. Yield 0.79 g crystals with m.p. 172-174°, or 50.4 % of the theoretical. After recrystallization from alcohol, the melting point increased to 175-176°.

Found %: N 10.03. $C_{17}H_{19}O_3N_2$. Calculated %: N 9.93.

2) From N-methyl- β -phenyl- β -alanylamine. 0.4 g of N-methyl- β -phenyl- β -alanylamine hydrochloride was introduced into a solution of 0.2 g of sodium hydroxide in 2 ml of water. 0.27 g of benzoyl chloride was added to the solution obtained. Upon shaking, crystals with m.p. 171-172° precipitated. After recrystallization from alcohol, 0.45 g of crystals with m.p. 175-176° were obtained. The yield was about 85.5 % of the theoretical.

A mixed melting point with the N-methyl-N-benzoyl- β -phenyl- β -alanyl amide obtained in the previous experiment did not give a depression.

SUMMARY

1. The conditions for the preparation of β -phenyl- β -(N-methylamino)propionic acid were studied.

2. The hydrochloride, ethyl ester, amide, and the N-nitroso derivative of β -phenyl- β -(N-methylamino)propionic acid were prepared to characterize it.

3. The benzylation of the phenylmethylamino acid was effected, and the synthesis of β -phenyl- β -(N-benzoyl-N-methylamino)propionamide was accomplished by two methods.

4. An attempt was made to synthesize 1-methyl-2,6-diphenyl-4-oxotetrahydropyrimidine by the dehydration of the benzoylamino acid amide by means of acetic anhydride and anhydrous oxalic acid, and it was shown that the formation of the pyrimidine derivative did not occur under these conditions.

5. The reaction of β -phenyl- β -(N-methylamino)propionamide and potassium hypobromite was studied, and it was found that 1-methyl-6-phenylglyoxalidone, which does not possess antibiotic activity, was obtained from this reaction in a 25% yield.

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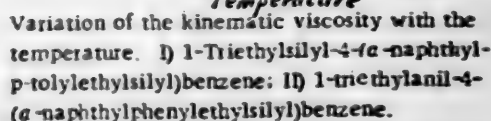
Received October 10, 1952.

P. S. Sanin

[illegible]

EXPERIMENTAL

70 g of α -naphthyltriethoxysilane, 108 g of bromophenyltriethylsilane, 12 g of magnesium, 1 g of iodine, 400 ml of ether, and 100 ml of toluene were used. An ether solution of bromophenyltriethylsilane was added in two portions to a mixture of the magnesium and the iodine in a flask equipped with a stirrer. Several minutes after the addition of the first half of the ether solution, an energetic reaction began which almost stopped within a half hour; then the second half of the ether solution of the bromophenyltriethylsilane was added, and the flask was heated on the water bath for 3 hours more at the end of the energetic reaction. The naphthyltriethoxysilane, diluted with ether (1:1) was added to the magnesium bromophenyltriethylsilane prepared in the above manner, and the reaction mass was heated for 1 hour on the water bath; the ether was then removed and replaced with toluene in which the heating was continued for 2 hours on the boiling water bath. Upon cooling the flask, the reaction mixture was treated with 20% NH_4Cl ; the upper layer which separated was removed from the aqueous solution after the addition of 50 ml of ether and the toluene, the residue (130 g) was vacuum distilled at 7 mm: 1) 65-130° (main part at 102-104°) - 28g; 2) 130-220° - 11g; 3)



The 1st fraction was shown to be phenyltriethylsilane upon investigation; it resulted from the decomposition of the unreacted magnesium bromophenyltriethylsilane with water.

The 2nd fraction was collected in the interval 242-245° (7 mm) upon redistillation: d_{20}^{20} 1.025.

0.1792 g substance: 0.4746 g CO₂; 0.1368 g H₂O. 0.6324 g substance: 0.1773 g SiO₂. 0.0570 g substance: 14.35 ml 0.1 N Na₂S₂O₃. Found %: C 72.22; H 8.54; Si 13.08; OC₂H₅ 18.86. C₂₁H₃₀Si₂O₂. Calculated %: C 71.50; H 8.31; Si 12.86; OC₂H₅ 20.64.

The increased amount of carbon and the decrease in the ethoxyl groups was caused, evidently, by the presence of impurities of the disilane (C₂H₅)₂SiC₆H₅Si(C₂H₅)₂, whose formation during the preparation of magnesium bromophenyltriethylsilane has been reported by Grütner and Krause [2].

1-Triethylsilyl-4-(α -naphthyl-p-tolyloxyethyl)silane. The following were used: the diethoxy derivative (I), 33 g, p-bromotoluene, 106 g, magnesium, 15 g, ether 300 ml, and toluene 100 ml. An ether solution (1:1) of the diethoxy derivative was added at room temperature to the p-tolyl magnesium bromide; after the replacement of the ether with toluene, the reaction mixture was heated for 3 hours on an oil bath to the boiling point of the toluene. The contents of the flask were diluted with water and 10 % sulfuric acid; the toluene solution was washed and dried after separation, and subjected to distillation; the residue (40 g) after the removal of the toluene was vacuum distilled. A fraction with b.p. 282-284° (7 mm) - 26 g (72%); d_{20}^{20} 1.0470 was isolated.

0.2608 g substance: 0.7438 g CO₂; 0.1880 g H₂O. 0.6424 g substance: 0.1632 g SiO₂. 0.0788 g substance: 8.57 ml 0.1 N Na₂S₂O₃. Found %: C 77.78; H 8.06; Si 11.85; OC₂H₅ 8.80. C₂₁H₂₈Si₂O. Calculated %: C 77.11; H 7.95; Si 11.63; OC₂H₅ 9.32.

1-Triethylsilyl-4-(α -naphthylphenylethoxysilyl)benzene was obtained from 33 g of the diethoxy derivative (I) under the above reported conditions in an 80 % yield in the form of a viscous yellow liquid with b.p. 274-276° (7 mm) and d_{20}^{20} 1.055.

0.2076 g substance: 0.5914 g CO₂; 0.1444 g H₂O. 0.5730 g substance: 0.1453 g SiO₂. 0.1048 g substance: 12.84 ml 0.1 N Na₂S₂O₃. Found %: C 77.69; H 7.78; Si 11.83; OC₂H₅ 8.90. C₂₀H₂₆Si₂O. Calculated %: C 76.80; H 7.75; Si 11.98; OC₂H₅ 9.61.

The following silicon hydrocarbons were synthesized by substituting alkyl groups for ethoxy groups in the ethoxy derivatives obtained under conditions reported for the preparation of monosilanes [1].

1-Triethylsilyl-4-(α -naphthyldiethylsilyl)benzene with a yield of 76 % of the theoretical: b.p. 249-252° (7 mm); d_{20}^{20} 0.9943.

0.1958 g substance: 0.5562 g CO₂; 0.1614 g H₂O. 0.6268 g substance: 0.1890 g SiO₂. Found %: C 72.47; H 9.22; Si 14.07. C₂₀H₂₆Si₂. Calculated %: C 72.15; H 8.97; Si 13.88.

1-Triethylsilyl-4-(α -naphthylphenylethylsilyl)benzene with a yield of 90 % of the theoretical: b.p. 276-278° (7 mm); d_{20}^{20} 1.0406.

0.2206 g substance: 0.6466 g CO₂; 0.1612 g H₂O. 0.6250 g substance: 0.1607 g SiO₂. Found %: C 79.84; H 8.17; Si 12.00. C₂₀H₂₆Si₂. Calculated %: C 79.57; H 8.02; Si 12.41.

1-Trimethylsilyl-4-(α -naphthyl-p-tolyloxyethyl)silane was obtained with a yield of 85 % of the theoretical: b.p. 284-286° (7 mm); d_{20}^{20} 1.035.

0.2246 g substance: 0.6568 g CO₂; 0.1700 g H₂O. 0.6022 g substance: 0.1379 g SiO₂. Found %: C 79.70; H 8.46; Si 10.67. C₂₁H₂₈Si₂. Calculated %: C 79.76; H 8.21; Si 12.03.

1-Triethylsilyl-4-(α -naphthyl-p-tolyl-n-butylsilyl)benzene was obtained with a yield of 60 % of the theoretical: b.p. 293-295° (7 mm); d_{20}^{20} 1.024.

0.2234 g substance: 0.6554 g CO₂; 0.1700 g H₂O. 0.7168 g substance: 0.1587 g SiO₂. Found %: C 80.01; H 8.51; Si 10.33. C₂₂H₃₀Si₂. Calculated %: C 80.08; H 8.56; Si 11.36.

The last three disilanes are thick, poorly mobile, yellow colored liquids.

The determination of the carbon and hydrogen for all of the compounds synthesized was effected by the combustion of the sample of the substance in a tube with copper oxide. The silicon was determined by means of oxidation with concentrated H₂SO₄ in the presence of K₂SO₄ and CuSO₄ and the ethoxy groups according to Kreshkov and Neissonova [4].

SUMMARY

The following were newly synthesized: 1-triethylsilyl-4-(α -naphthyl-diethoxysilyl)benzene, 1-triethylsilyl-4-(α -naphthyl-*p*-tolylethoxysilyl)benzene, 1-triethylsilyl-4-(α -naphthylphenylethoxysilyl)benzene, and the silicon hydrocarbons: 1-triethylsilyl-4-(α -naphthyl-diethylsilyl)benzene, 1-triethylsilyl-4-(α -naphthylphenylethylsilyl)benzene, 1-triethylsilyl-4-(α -naphthyl-*p*-tolylethylsilyl)benzene, 1-triethylsilyl-4-(α -naphthyl-*p*-tolyl-*n*-butylsilyl)benzene.

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Received January 3, 1953

• See Consultants Bureau Translation, p. 1167.



A NEW METHOD FOR THE SYNTHESIS OF ORTHO DERIVATIVES OF BENZOTRIFLUORIDE

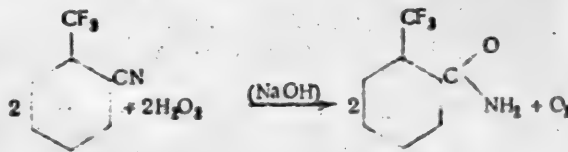
L. M. Yagupolsky and N. I. Manko

The trifluoromethyl group is an electropositive meta-directing group; for this reason, the meta derivatives of benzotrifluoride have been the most accessible and investigated. A method for the synthesis of para derivatives has also been reported [1]. The ortho-substituted benzotrifluorides have remained the least accessible. Up to now, they were prepared by means of o-aminobenzotrifluoride [1].

In 1951, a method for the preparation of o-bromobenzotrifluoride was reported which consisted of the metalization of benzotrifluoride with butyl lithium followed by the substitution of the lithium by bromide [2]. The yield of o-bromobenzotrifluoride was 28% of the theoretical. o-Trifluoromethylbenzoic acid was prepared from it. The low yield of o-bromobenzotrifluoride, and the complexity of its preparation, lowers the value of the above method.

The authors decided to try and find a simpler and more convenient method for the synthesis of o-derivatives of benzotrifluoride. The possibility for the preparation of o-trifluoromethylbenzotrifluoride from the corresponding trichloromethyl derivative [3] was investigated for this purpose. The fluorination of o-trichloromethylbenzotrifluoride with antimony trifluoride was found to proceed smoothly with a yield of 78%. This made possible its use as a starting material for the synthesis of ortho derivatives of benzotrifluoride.

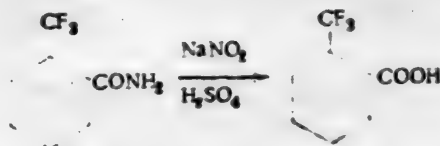
o-Trifluoromethylbenzotrifluoride is reported in the literature. It was prepared from the corresponding, difficultly accessible, amine in low yield. It, evidently, was not isolated in the pure form. The reported m.p. +7.5° [4] is incorrect; an m.p. +18° was found. Several derivatives were obtained from o-trifluoromethylbenzotrifluoride. These substances were known previously. However, the methods used by the authors for their synthesis were simpler and gave considerably better yields. Thus o-trifluoromethylbenzamide was prepared in an 87% of the theoretical yield from o-trifluoromethylbenzotrifluoride by the action of 30% hydrogen peroxide, in the presence of alkali, on an alcoholic solution of the nitrile, according to Radziszewski [5].



The amide of o-trifluoromethylbenzoic acid was previously prepared by heating its methyl ester for 36 hours at 110° in a sealed tube with concentrated ammonia solution, [6].

o-Trifluoromethylaniline, which previously served as starting substance for the synthesis of ortho derivatives of benzotrifluoride, was obtained in a yield of 72% of the theoretical from o-trifluoromethylbenzamide by the Hoffman reaction.

o-Trifluoromethylbenzoic acid was previously synthesized (in addition to the above reported method with the aid of lithium organo-compound) by boiling the nitrile with 10% sodium hydroxide for 80 hours [6]. A considerable amount of phthalic acid was also obtained. o-Trifluoromethylbenzoic acid was obtained from its amide by Bouveault's method [7]:



The hydrazide, unreported in the literature, was obtained from ethyl o-trifluoromethylbenzoate which was synthesized by the authors, by boiling it for many hours with hydrazine hydrate.

The above difficulty in converting ethyltrifluoromethylbenzoate into the hydrazide, as well as the difficulty mentioned in the literature in preparing the methyl ester (two day boiling of the acid with hydrogen chloride in methyl alcohol [6]) and the amide [6], indicates, evidently, that the CF_3 group causes steric hindrance.

EXPERIMENTAL

o-Trichloromethylbenzonitrile [3]. 20 g of o-tolynitrile prepared from o-toluidine [8] was placed into a 100 ml round bottom flask equipped with a two necked adapter. A bubbler was introduced through one of the necks and the other one was connected to a condenser protected by calcium chloride tube. The flask was heated on an oil bath to 150° , illuminated by a mercury lamp, and chlorine was passed in through the bubbler until an increase in weight of 17 g. The oil bath temperature was gradually increased to 185° during the process of chlorination. The reaction mass was vacuum distilled. Two fractions were collected: 1) up to a constant boiling point at 8 mm, 11.2 g, 2) b.p. $151-152^\circ$ at 8 mm, 22.16 g. Both fractions crystallized at the same time. M.p. of Fraction 1, $85-87^\circ$. Melting point of Fraction 2, $94-95^\circ$, corresponding to that reported in the literature [3] for o-trichloromethylbenzonitrile. 10.1 g of the product with m.p. $94-95^\circ$ was isolated from Fraction 1 after recrystallization from alcohol. The total yield was 35.26 g or 86% of the theoretical.

o-Trifluoromethylbenzonitrile. 20 g of o-trichloromethylbenzonitrile was mixed with 20 g of antimony trifluoride in a 100 ml Wurtz flask. The mixture was heated until a homogenous liquid formed and distilled. The distillate was dissolved in a mixture of ether and 6 N hydrochloric acid, the ether layer was washed several times with 6 N hydrochloric acid until complete removal of the SbCl_3 , then 1-2 times with water, and dried over anhydrous Na_2SO_4 . The ether was removed and the residue distilled. B.p. $204-206^\circ$. Yield 11.9 g. The substance readily crystallized in an ice bath and had an m.p. 18° . Found %: N 8.28, 8.22. $\text{C}_7\text{H}_4\text{NF}_3$. Calculated %: N 8.18.

o-Trifluoromethylbenzamide. 13 g of o-trifluoromethylbenzonitrile, 50 ml of 95% ethyl alcohol, 33 ml of 30% hydrogen peroxide, and 5 ml of 6 N sodium hydroxide were placed into a 250 ml round bottom flask. The mixture started to evolve oxygen at once. The reaction was accompanied by a strong evolution of heat. The temperature was kept at $40-50^\circ$ by external cooling. The exothermic reaction moderated noticeably after 1 hour, and the mixture was left to stand overnight. The mixture was then heated for 3 hours to 50° on the water bath and then cooled to 0° . The precipitated crystals were filtered, washed with water, and dried (11 g). M.p. $160-161^\circ$, which coincides with that reported in the literature [6]. The filtrate was diluted with an equal volume of water and again cooled to 0° ; 1.5 g more of the amide with m.p. 160° formed. Total yield, 12.5 g.

o-Trifluoromethylaniline. A solution of 10 g of sodium hydroxide in 80 ml of water was cooled to 0° , and 2.5 ml of bromine was added to it. The cold solution of sodium hypobromite was added to 8 g well pulverized o-trifluoromethylbenzamide in a 150 ml flask. The mixture was mixed until complete solution of the amide and placed on a boiling water bath. The heating was continued for 45 minutes, and the flask was cooled to room temperature. The amine was extracted with three 15 ml portions of ether, the combined ether extracts were dried with anhydrous Na_2SO_4 , the ether removed, and the o-trifluoromethylaniline vacuum distilled. M.p. $65-67^\circ$ at 15 mm. Yield 4.9 g. The acetyl derivative, obtained from the amine and acetic anhydride in pyridine, had an m.p. $94-95^\circ$ (reported in the literature, m.p. 94.5° [6]).

o-Trifluoromethylbenzoic acid. 14.4 g of o-trifluoromethylbenzamide was suspended in 72 ml of water in a 500 ml three necked flask equipped with stirrer, thermometer and dropping funnel whose tip was drawn into a capillary going to the bottom of the flask. 36 ml of concentrated sulfuric acid was added to the mixture with stirring. The mixture was heated to 98° . The amide dissolved completely. 12 g of sodium nitrite in 180 ml of water was added to the solution with efficient stirring from the dropping funnel. The temperature of the reaction mixture was kept at $98-100^\circ$; it was necessary to heat the flask from time to time. After the addition of NaNO_2 solution, the flask was cooled with cold water, and the acid extracted from the solution with three 25 ml portions of ether. The combined ether extracts were shaken with a solution of sodium hydroxide. The aqueous layer was separated and acidified with concentrated hydrochloric acid. The precipitated o-trifluoromethylbenzoic acid was filtered, washed with water, and dried. Yield 13.2 g or 91% of the theoretical. M.p. $107-108^\circ$ (an m.p. 108.5° [6] is given in the literature).

The ethylester of o-trifluoromethylbenzoic acid was prepared by heating the acid chloride with absolute ethyl alcohol. The product was washed with water, dried over Na_2SO_4 , and vacuum distilled. B.p. $90-91^\circ$ at 10 mm.

o-Trifluoromethylbenzoic hydrazide was prepared by boiling the ethyl ester of this acid with hydrazine for 3 hours. The product was recrystallized from aqueous alcohol. M.p. 134°.

Found %: N 13.55, 13.63. $C_8H_5ON_2F_3$. Calculated %: N 13.72.

SUMMARY

A new way of synthesizing ortho derivatives of benzotrifluoride has been found, making it possible to prepare *o*-trifluoromethylbenzonitrile, *o*-trifluoromethylbenzoic acid, and *o*-trifluoromethylaniline, while it may also be employed in the preparation of other compounds not described hitherto.

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Received January 21, 1963.

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SYNTHESIS OF CYCLOHEPTANE DERIVATIVES WITH THE AID OF ACETOACETIC ESTER

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In one of the previous communications [1], it was shown that, if the reaction for the formation of cycloheptane-1,1-dicarboxylic ester with the aid of malonic ester was conducted in two stages, the yield of the substance was considerably increased. Cycloheptane-1,1-dicarboxylic acid, previously unreported in the literature, was obtained by saponifying it. It appeared to be of interest to also try and prepare seven membered rings with the aid of acetoacetic ester since, as far as it is known, the given reaction has not been studied by anyone up to now.

For this purpose, ζ -iodohexylacetoacetic ester (I), unreported up to now, was initially synthesized in the present investigation by the action of sodio acetoacetic ester on hexamethylene iodide.



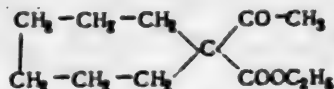
(I)

The yield of the above compound, as it had been previously shown with other examples [2], varied with the amount of the dihalo derivative used in each separate case. Thus for example, if 1 g atom of metallic sodium (in the form of the alcoholate), 4 moles of acetoacetic ester, and 1 mole of hexamethylene iodide were used for the reaction, ζ -iodohexylacetoacetic ester was obtained in a yield of 33.1% of the theoretical. If the amount of hexamethylene iodide used was 2 times greater than required by calculations, then the yield of the haloalkylacetoacetic ester was increased to 65.4% of the theoretical.

With a 3 fold quantity of the dihalo derivative, ζ -iodohexylacetoacetic ester was formed with a yield equal to 74.7% of the theoretical.

The yields, calculated on the basis of previously given theoretical considerations [2], were equal to 36.6, 60.4, and 72.4%, respectively, of theory. Therefore, there is a satisfactory agreement of the yields obtained experimentally in the given case with those calculated on the basis of the law of mass action.

The second stage of the reaction, i.e., the cyclization of ζ -iodohexylacetoacetic ester (I), was conducted in dilute (0.22 molar) alcoholic solution. It was found that the normal reaction product, 1-acetylcycloheptane-1-carboxylic ester (II), formed in a yield of about 32% of theory was subjected to alcoholysis to a considerable extent with the formation of acetoacetic ester and the ethyl ester of cycloheptanecarboxylic acid.



(II)

For this reason, a mixture was formed in the end which consisted of the ethyl ester of cycloheptanecarboxylic acid (yield 25.5% of the theoretical) and 1-acetylcycloheptane-1-carboxylic ester (yield about 6%). The latter compound was characterized by means of its semicarbazone. In addition, a large amount of high molecular condensation products was obtained.

The alcoholysis of dialkylated esters of β -keto acids under the catalytic effect of alcoholate has been observed many times in the past [3]. The cleavage of 1-acetylcyclopentane-1-carboxylic ester formed by the action of sodio acetoacetic ester on tetramethylene bromide [4], was also found to occur with the formation of the ethyl ester of cyclopentanecarboxylic acid by the effect of sodium alcoholate.

EXPERIMENTAL

The hexamethylene iodide necessary for the investigation was prepared by means of a previously reported method [1] and had a b.p. 135-138° at 6 mm.

ζ -Iodoethylacetoacetic ester. 4.6 g (0.2 g atoms) of metallic sodium was dissolved in 75 ml of absolute alcohol, and then 104 g (0.8 mole) of freshly distilled acetoacetic ester (b.p. 70° at 13 mm) followed by 203 g (0.6 mole) of hexamethylene iodide was added to the alcoholate solution. After heating the reaction mixture to boiling on a bath for 4 hours and cooling, the reaction product was poured into water and extracted with ether. The ether extracts were washed with a weak solution of hyposulfite, dried with fused calcium chloride, the ether was then removed, and the residue fractionated in vacuum. 125 g of hexamethylene iodide was recovered (a fraction with b.p. 132-139° at 6 mm), and 58 g of a fraction with b.p. 155-186° (mainly at 168-177°) at 6 mm was obtained. Upon redistillation of this fraction, an average of 50.6 g (74.4% of the theoretical) of a colorless oily liquid which rapidly yellowed, was isolated at 152-156° (1.5 mm); d_4^{20} 1.3607; n_D^{20} 1.4947; M_R 72.82. $C_{12}H_{21}O_3I$. Calculated: for the enolic form 73.32; for the ketonic 72.18, average 72.75.

0.3481 g substance: 0.5452 g CO_2 ; 0.1965 g H_2O . 0.3281 g substance: 0.2274 g AgI (according to Carius). Found %: C 42.71; H 6.28; I 37.46. $C_{12}H_{21}O_3I$. Calculated %: C 42.35; H 6.18; I 37.35.

In a second experiment, 44.5 g (65.4%), of ζ -iodoethylacetoacetic ester was obtained from 4.6 g (0.2 g-atom) of sodium, dissolved in 75 ml of absolute alcohol, 104 g (0.8 mole) of acetoacetic ester, and 135 g (0.4 mole) of hexamethylene iodide.

In a third experiment, 22.5 g or 33.1% of the theoretical of ζ -iodoethylacetoacetic ester was obtained with the use of the theoretical amount (68 g or 0.2 mole) of hexamethylene iodide.

Cyclization of ζ -iodoethylacetoacetic ester. 3.45 g (0.15 g atom) of metallic sodium was dissolved in 650 ml of absolute alcohol, 51 g (0.15 mole) of ζ -iodoethylacetoacetic ester was added, and the mixture was heated for 3 hours to boiling. The main part of the alcohol was distilled off (a distinct odor of acetoacetic ester was detected in the distillate), the residue was poured into water, the reaction products extracted with ether, the ether extracts washed with a dilute hyposulfate solution, dried with fused $CaCl_2$, the ether removed, and the residue fractionated in vacuum. 6.5 g of a substance boiling at 72-76° at 3 mm and 2 g of fraction with b.p. 102-104° at 2 mm were obtained. A large amount of a thick residue remained in the flask. The fraction with b.p. 72-75° upon redistillation, boiled mainly at 74° at 3 mm and was the ethyl ester of cycloheptane carboxylic acid. (Yield 25.5% of the theoretical).

d_4^{20} 0.9515; n_D^{20} 1.4482; M_R 47.84; Calc. 47.83.

0.2234 g substance: 0.5758 g CO_2 ; 0.2165 g H_2O . Found %: C 70.29; H 10.76. $C_{11}H_{19}O_2$. Calculated %: C 70.59; H 10.59.

6 g of the cycloheptanecarboxylic ester was saponified with an aqueous alcoholic potassium hydroxide solution, the alcohol removed, the residue acidified with sulfuric acid, and the precipitated liquid acid extracted with ether. The ether extracts, dried with fused $CaCl_2$, left an acid, after the removal of the solvent, which was distilled at ordinary pressure (709 mm) where it boiled at 248-251° [5]. Yield was 3.9 g (78% of the theoretical).

The amide of cycloheptanecarboxylic acid obtained in the usual manner [1] (by means of the acid chloride), melted at 195-196° [5] after 2 recrystallizations from dilute alcohol. The fraction with b.p. 102-104°, according to constants and results of elementary analysis, was the not completely pure ester of 1-acetylcycloheptane-1-carboxylic acid. For this reason, it was treated in the cold with a solution of semicarbazide. The separation of crystals started on the following day. Several days later, the crystals were filtered and twice recrystallized from alcohol, after which they melted at 193-194°.

0.1122 g substance: 0.2392 g CO_2 ; 0.0900 g H_2O . 0.0865 g substance: 9.55 ml 0.1 NH_4SO_4 (according to Kjeldahl). Found %: C 58.05; H 8.91; N 15.46. $C_{11}H_{21}O_3N_3$. Calculated %: C 58.00; H 8.55; N 15.61.

SUMMARY

1. ζ -Iodoethylacetoacetic ester was obtained by the action of sodio acetoacetic ester on hexamethylene iodide. By using 1 mole of hexamethylene iodide for 1 mole of sodium alcoholate and 4 moles of acetoacetic ester, the yield of ζ -iodoethylacetoacetic ester was equal to 33.1% of the theoretical. By using twice the

theoretical amount of hexamethylene iodide, the yield of the reaction product was 65.4% and with a 3-fold amount, 74.4% of the theoretical. The yields obtained agree satisfactorily with those calculated on the basis of the mass action law.

2. Upon cyclization of γ -iodohexylacetylacetic ester with the aid of sodium alcoholate in an 0.22 molar alcoholic solution, 1-acetylcycloheptane-1-carboxylic ester was formed in a yield of about 33% of the theoretical. During the process of the reaction it was subjected to alcoholysis to a considerable degree and was converted into the ethyl ester of cycloheptanecarboxylic acid.

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Received July 29, 1952

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** See Consultants Bureau Translation, p. 1993.



INVESTIGATION OF THE PROCESS OF ISOMERIZATION AND DIMERIZATION OF DIMETHYLVINYLCARBINOL IN RELATION TO THE pH OF THE REAGENT

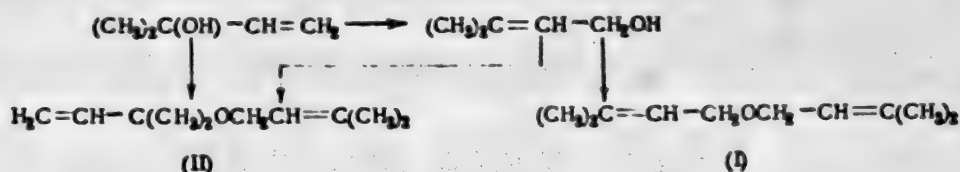
II. ACTION OF A SATURATED SOLUTION OF CUPROUS CHLORIDE IN HYDROCHLORIC ACID ON DIMETHYLVINYLCARBINOL

A. I. Lebedeva and L. F. Almashi

From previously published communications it is known [1,2,3] that sulfuric acid causes dehydration, allylic rearrangement, and condensation of dimethylvinylcarbinol, as a result of which are formed isoprene, primary γ,γ -dimethylallylic alcohol, linalool, geraniol, and terpin hydrate. In the previous communication, A. I. Lebedeva and L. L. Shchukovskaya [4] reported the start of an investigation of the various transformations of dimethylvinylcarbinol in relation to the pH of the acting reagent. In the present investigation, it was decided to continue this investigation at higher hydrogen ion concentrations and to study the action of a saturated solution of cuprous chloride in hydrochloric acid of various concentrations: 1 N, 5 N, and 10 N on dimethylvinylcarbinol. It was found that under the conditions investigated, the removal of water occurs not only from one molecule of the alcohol with the formation of isoprene, but also from two molecules, leading to formation of ethers of dimethylvinylcarbinol and γ,γ -dimethylallylic alcohol, isomeric with it, γ,γ -dimethylallylic ether of 2-methyl-2-butene-4-ol (I) and γ,γ -dimethylallylic ether of 2-methyl-3-butene-2-ol (II).

On the basis of the experiments conducted, it cannot be stated with complete certainty that the formation of the ethers occurs by means of a chloride stage with the subsequent cleavage of HCl from a molecule of the chloride and the alcohol, but a possibility for this occurrence exists. It is known from I. N. Nazarov and L. N. Azerbaeva's [5] investigation that the replacement of a hydroxyl by a chlorine occurs very readily even at 0° by the action of gaseous hydrogen chloride on dimethylvinylcarbinol resulting in a mixture of primary and tertiary chlorides.

The reaction forming the unsaturated ethers from dimethylvinylcarbinol can be represented schematically in the following manner:



From the results obtained (Table 1), it can be seen that decreasing the pH of the solution of cuprous chloride leads to the increase in the yield of the primary-primary ether, and conversely, the yield of the primary-tertiary ether is increased with the increase in pH. These findings correspond to the results of I. N. Nazarov and co-workers [6] on the obtaining of methyl ethers from dimethylvinylcarbinol; it was shown that the ratio of the isomeric ethers depends on the concentration of sulfuric acid.

A complex mixture was obtained as a result of a several-day action of the above solution of cuprous chloride in hydrochloric acid on dimethylvinylcarbinol, from several individual compounds (1-5) were isolated upon many redistillations through a column, having the following boiling points: 1) 34-36°, 2) 97-98°, 3) 49° (10 mm), 4) 40° (3 mm), 5) 55° (3 mm) (Table 1). The higher boiling fraction has not been investigated further as yet. Compound 1 corresponds to isoprene according to its constants, 2, starting dimethylvinylcarbinol, 3 primary γ,γ -dimethylallylic alcohol.

The structure of compound 4 with b.p. 40° (3 mm) was determined by ozonolysis, study of Raman spectra, and catalytic hydrogenation in the presence of platinum.

The investigation of the ozonolysis products did not give any definite results even if it is assumed that the ozonolysis occurs according to the scheme given by Ya. M. Siobodin [7] for substances having an allylic group in their composition; for this reason a Raman spectrum was taken for the substance. A photograph of the Raman spectrum is given in the Figure. (See Plate, page 1115).

It is known [8, 9] that the frequency 1675 cm^{-1} is characteristic for secondary-tertiary double bonds, frequency 1640 cm^{-1} for primary-secondary double bonds, and 1413 cm^{-1} for an end methylene group.

The catalytic hydrogenation of compound 4 in the presence of platinum black at room temperature and atmospheric pressure was of great interest. Under these conditions, the cleavage of this compound with hydrogen occurred with the formation of isopentane, amylene hydrate, and primary isoamyl alcohol. 3 molecules of hydrogen were consumed for each molecule of the compound consumed even though it only had 2 double bonds (which was determined by the bromine number).

It was found that after the addition of one molecule of hydrogen, the bromine number decreases (which is apparent from the number of milliliters of bromide-bromate consumed for the titration), and a hydroxyl appears.

The hydrogenation under the given conditions does not occur selectively: simultaneously with the addition of hydrogen at the double bond, a cleavage of the ether bond occurs with the formation of compounds containing a hydroxyl (Table 2).

The absence of a positive reaction for a hydroxyl and carbonyl group, with the presence of one atom of oxygen in the molecule, the investigation of the Raman spectrum, and the results of the catalytic hydrogenation meant that compound 4 must have been the γ,γ -dimethylallylic ether of 2-methyl-3-butene-2-ol (II).

The cleavage of the ether bond under such mild conditions is only reported in one paper [10], in which the authors were able to cleave an ether bond with phenyl radicals during hydrogenation over platinum oxide in glacial acetic acid.

Compound 5 had a very sharp odor, which caused a headache. The analyses showed that the compound had a general formula $\text{C}_{11}\text{H}_{18}\text{O}$. The hydroxyl determination according to Terentyev-Shcherbakova, gave negative results. The substance was hydrogenated catalytically in the presence of platinum black in absolute ether. More than three molecules of hydrogen were absorbed per molecule of the compound. A mixture was obtained as a result of the hydrogenation from which the following compounds were isolated and characterized: isopentane, primary isoamyl alcohol, and diisoamyl ether.

On the basis of all the given determinations, it could be considered that compound 5 was γ,γ -dimethylallyl 2-methyl-2-butene-4-yl ether.

Therefore, unsaturated ethers were obtained from dimethylvinylcarbinol and it was shown that the ether bond in the compounds of the above structure was readily cleaved with hydrogen in the presence of platinum black at atmospheric pressure and room temperature.

EXPERIMENTAL

Technical dimethylvinylcarbinol, b.p. 96-97° containing about 85% of the pure substance was used for all experiments. The percent content of dimethylvinylcarbinol was determined by catalytic hydrogenation in the presence of platinum black and bromination with an aqueous solution of bromide-bromate. The total concentration of hydrochloric acid was the same for each experiment, only the concentration of the solution used was varied. The solution of hydrochloric acid used for the experiment was saturated with cuprous chloride by prolonged shaking. The pH of the solution was determined prior to and after saturation with glass electrodes. The experiments were conducted in a three-necked flask equipped with a stirrer, dropping funnel, and a long reflux condenser. The solution of cuprous chloride in hydrochloric acid was added slowly with stirring to the dimethylvinylcarbinol in the

flask. 50 g of dimethylvinylcarbinol were used for every experiment. The mixture was stirred efficiently for 60 hours at room temperature, 3 hours at 30-40°, and 3 hours at 70-80°. The upper and lower layers were then separated, the upper layer was washed with aqueous sodium carbonate solution, and dried with fused potassium carbonate. After drying, the upper layer was separated into several fractions by simple distillation which were then each subjected to fractional distillation on a column fitted with a complete condensation head. The lower layer was extracted with ether for 48 hours in a percolator. Only a small amount of dimethylvinylcarbinol was isolated from the lower layer after the removal of the ether; it did not contain any other products. The results of the experiments conducted are given in Table 1.

TABLE 1

Exp. No.	Amt. of saturated cuprous chloride in hydrochloric acid used for the reaction (in g)	Concentration hydrochloric acid used for the reaction	pH of the hydrochloric acid	pH of the saturated cuprous chloride solution in hydrochloric acid	Yield of substance with b.p. 34-36° (in g)	Yield of substance with b.p. 97-98° (in g)	Yield of substance with b.p. 40° (10 mm) (in g)	Yield of substance with b.p. 40° (3mm) (in g)	Yield of substance with b.p. 55° (3mm) (in g)	Yield of substance with b.p. 74-76° (10 mm) (in g)	Residue in distillation flask (in g)
1	50	1 N	-0.05	-0.15	2.0	10.2	4.0	9.0	1.5	1.0	2.5
2	10	5 N	-0.43	-0.55	4.0	10.0	6.5	5.0	1.5	—	8.0*
3	5	10 N	-0.73	-1.1	2.0	15.0	2.0	7.5	3.1	5.5	12.0

* In this experiment, the fraction with b.p. 74-76° (3 mm) was not isolated.

Analysis of Fraction 1 with b.p. 34-36°

n_D^{17} 1.4150; d_4^{17} 0.6805; MR_D 25.05. $C_3H_5F_2$. Calculated 24.33.

Analysis of Fraction 2 with b.p. 97-98°

n_D^{24} 1.4110; d_4^{24} 0.8097; MR_D 26.42. C_3H_5OF . Calculated 26.35.

Analysis of Fraction 3 with b.p. 40° (10 mm)

n_D^{28} 1.4410; d_4^{28} 0.8680; MR_D 26.21. C_3H_5OF . Calculated 26.35.

0.2107 g substance: 16.4 g benzene Δt 0.80°. 0.1050 g substance: 28.5 ml CH_4 (20°, 761.2 mm).
Found: M 81.91; number of active H 0.95. C_3H_5O . Calculated: M 86.16; number of active H 1.00.

Analysis of Fraction 4 with b.p. 40° (3mm)

The compound had a pleasant odor, its optimum yield was about 30 % based on the dimethylvinylcarbinol reacted.

n_D^{16} 1.4423; n_D^{16} 1.4399; n_D^{16} 1.4503; d_4^{16} 0.8332; MR_D 48.92; MR_g 48.74; MR_B 49.69.

$C_{11}H_{12}OF_2$. Calculated: MR_D 49.26; MR_g 48.80; MR_B 49.75.

0.1028 g substance: 0.2923 g CO_2 ; 0.1067 g H_2O . 0.1270 g substance: 0.3613 g CO_2 ; 0.1308 g H_2O .
0.2281 g substance: 15.3 g benzene: Δt 0.50°. 0.2100 g substance: 24.5 ml bromide-bromate (T 0.01732 g/ml).
Found %: C 77.61, 77.64; H 11.61, 11.52; M 151.6. Bromine number 312. $C_{11}H_{12}O$. Calculated: C 77.87; H 11.76; M 154.22. Bromine number 319.66.

2 g of the substance was ozonized in chloroform solution (30 ml) at -70° . 1.5 g of ozone added; 2.7 g of the ozonide remained after the filtration of the chloroform. The ozonide was decomposed with water, and the solution obtained was diluted to 500 ml with water.

Formic acid was determined in 50 ml of the solution by Finke's [11] method. 1.2790 g of Hg_2Cl_2 was obtained. Formaldehyde was determined in another 50 ml with dimedon. The weight of the dimedon derivative obtained was 0.0588 g, m.p. $188-189^{\circ}$. The total amount was 1.4 g based on the formic acid. About three molecules of formic acid were formed for a molecule of the compound. Potassium carbonate was added to a distinctly alkaline reaction to the solution remaining after the removal of the formaldehyde with dimedon. The neutral product then steam distilled into a sulfuric acid solution of 2,4-dinitrophenylhydrazine. The melting point of the 2,4-dinitrophenylhydrazone obtained was $125-126^{\circ}$. A mixed melting point with authentic acetone 2,4-dinitrophenylhydrazone gave no depression. Other neutral products were not detected. The rest of the solution was then worked up in the usual manner to isolate, first, the volatile acids, and then the non-volatile acids. None of these was found in the ozonolysis products.

The Raman spectrum of the compound was taken at an exposure of 1.5 hours and slit of 0.1 mm. A blue ($\lambda = 22938 \text{ cm}^{-1}$) line was used as the excitation line. The following frequencies (cm^{-1}) were obtained: (the intensities were evaluated visually and their relative values are given in the parentheses): 300 (2); 454 (1); 437 (5); 822 (2); 883 (3); 926 (4); 1044 (2); 1116 (0.5); 1154 (0.5); 1239 (1); 1247 (0.25); 1294 (3); 1326 (2); 1379 (6); 1413 (1.5); 1446 (6); 1640 (4); 1675 (6); 2793 (7); 2866 (1); 2923 (4); 2993 (1); 3046 (0.5); 3138 (0.25).

Catalytic hydrogenation of compound 4. 7.57 g of the substance; 0.8 g of Pt, 30 ml of absolute ether 3526 ml of H_2 (15° , 763 mm) was absorbed, 100.8 % of the theoretical (if 3 molecules of hydrogen are assumed).

The solution, after the filtration of the platinum, was distilled. The fraction boiling within the limits $30-36^{\circ}$ was shaken with concentrated hydrochloric acid in a separatory funnel; the upper layer was separated from the hydrochloric acid ether solution, washed with sodium carbonate solution, dried with CaCl_2 , and was distilled; a fraction boiling at $31-32^{\circ}$ (1.0 g) was collected

$$n_D^{20} 1.3540; d_4^{20} 0.6193; MR_D 25.31. \text{ Calculated } 25.29.$$

0.2570 g substance; 16.8 g benzene; $\Delta t 1.65^{\circ}$. Found: M 67.23. C_5H_{12} . Calculated: M 72.1.

The data obtained corresponded to isopentane.

Two individual compounds were isolated from the substance remaining after the distillation of the ether, by distilling it through a column with a complete condensation head; the first with b.p. $101-102^{\circ}$ (1.6 g)

$$n_D^{20} 1.4055; d_4^{20} 0.8062; MR_D 26.81; \text{ Calculated } 26.82.$$

0.0917 g substance; 24.8 ml CH_4 (20° , 759 mm). Found: number of active H 0.97. $\text{C}_5\text{H}_{11}\text{OH}$. Calculated: number of active H 1.00.

The qualitative Denige reaction (formation of a yellow precipitate) characteristic for tertiary alcohols was positive.

The data obtained corresponded to tertiary amyl alcohol, amylene hydrate.

The second compound boiled at $131-132^{\circ}$ (0.5 g).

$$n_D^{20} 1.4080; d_4^{20} 0.8132; MR_D 26.75; \text{ Calculated } 26.82.$$

0.0901 g substance; 25.0 ml CH_4 (17° , 761 mm). Found: number of active H 1.00. $\text{C}_5\text{H}_{11}\text{OH}$. Calculated: number of active H 1.00.

The theoretical amount of an α -naphthylurethane with m.p. $67-68^{\circ}$ was obtained from 0.3 g of the compound, which corresponded to the melting point of primary isoamyl alcohol α -naphthylurethane.

3 g of compound 4 was dissolved in 60 ml of absolute ether and hydrogenated catalytically in the presence of 0.3 g of Pt black. 2 ml samples were removed from the solution and the amount of bromide-bromate necessary to titrate it and the amount of methane separated during the determination of the hydroxyl measured. The analysis was conducted with the starting substance after the addition of one molecule of hydrogen, after the addition of two molecules, and finally, after the addition of three molecules.

The results of the analyses are given in Table 2.

TABLE 2

Name of Sample	Amount of bromide- bromate (in ml)	Amount of CH ₄ (in ml)
Starting substance	12.5	0
After addition of one molecule of hydrogen	9.1	6.9
After addition of two molecules of hydrogen	2.9	13.5
After addition of three molecules of hydrogen	0	15.5

Analysis of Fraction 5 with b.p. 55° (3 mm)

The compound had a very sharp odor, its optimum yield was about 16% based on the amount of dimethylvinylcarbinol reacted.

n_D^{16} 1.4500; n_D^{16} 1.4437; d_4^{16} 0.8380; MR_D 49.45;

MR_d 48.85. $C_{10}H_{18}O$. Calculated MR_D 49.26;

MR_d 48.80.

0.1220 g substance: 0.3474 g CO₂; 0.1263 g H₂O. 0.1230 g substance: 0.3501 g CO₂; 0.1271 g H₂O. 0.2611 g substance: 14.17 g benzene: Δt 0.630°. Found %: C 77.70, 77.68; H 11.59, 11.57; M 151.5. $C_{10}H_{18}O$. Calculated: C 77.87; H 11.76; M 154.2.

A negative reaction was obtained upon the determination of the hydroxyl according to Teremyev-Shcherbakova.

Catalytic hydrogenation of compound 5. 3.35 g of the substance, 0.3 g Pt, 30 ml of absolute ether. 1900 ml of H₂ was consumed (18°, 759 mm), 122% of the theoretical (based upon 3 molecules of hydrogen).

The solution was processed in the same manner as for the hydrogenation of compound 4. The first fraction boiling at 31-32° corresponded to isopentane. The second boiling at 131-132° (0.5 g) gave an α -naphthylurethane with m.p. 67-68° corresponding to primary isoamyl alcohol. The third fraction (0.4 g) boiled at 173-175°, n_D^{17} 1.4100.

0.2000 g substance: 15.2 g benzene: Δt 0.43°. Found: M 156.3. $C_{10}H_{22}O$. Calculated: M 158.3.

The data corresponded to diisoamyl ether.

SUMMARY

1. A saturated solution of cuprous chloride in hydrochloric acid (having a pH of 0.15 to 1.1) acts under determined conditions upon dimethylvinylcarbinol in such a manner that an allylic rearrangement and the dehydration of dimethylvinylcarbinol occurs with the formation of, in addition to isoprene and γ,γ -dimethylallyl alcohol two unsaturated ethers, γ,γ -dimethylallyl ether of 2-methyl-3-butene-2-ol (II) and γ,γ -dimethylallyl ether of 2-methyl-2-butene-4-ol (I).

2. A cleavage of the ether linkage occurred upon the catalytic hydrogenation of γ,γ -dimethylallyl ether of 2-methyl-3-butene-2-ol and γ,γ -dimethylallyl ether of 2-methyl-2-butene-4-ol at normal pressure and room temperature in the presence of platinum black with the formation of the corresponding amyl alcohols and the unsaturated hydrocarbon, isopentane.

3. The hydrogenation does not occur selectively under the given conditions. Simultaneously with the addition of the hydrogen to the double bond, occurs the cleavage of the ether linkage, and the formation of compounds containing a hydroxyl.

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Received July 25, 1952

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INVESTIGATION OF COMPOUNDS CONTAINING A THREE MEMBERED OXIDE RING

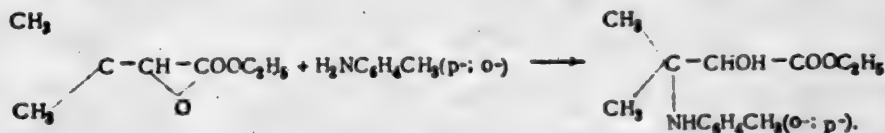
V. REACTION OF ETHYL β,β' -DIMETHYLGLYCIDATE WITH *o*- AND *p*-TOLUIDINE

V. F. Martynov

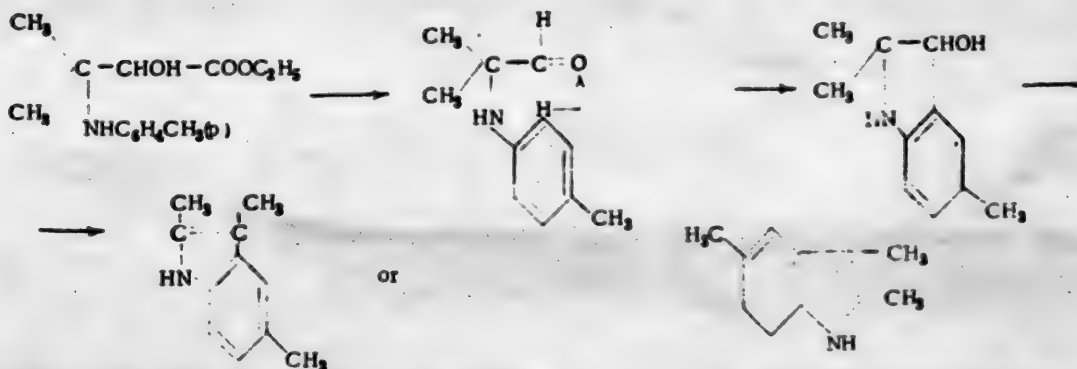
In the previous communication it was shown that the addition of aniline to ethyl β,β' -dimethylglycidate occurs with the formation of ethyl α -hydroxy- β -anilinoisovalerate. This means that the opening of the oxide ring of glycidic acid by the action of an aromatic amine occurs at the side of the β -carbon atom.

In view of the fact that these results were found to be in opposition to those of other authors [1], it was decided to prove the correctness of these conclusions upon other examples. For this purpose, the structures of the products of the reaction of *o*- and *p*-toluidine with ethyl β,β' -dimethylglycidate were investigated. The above products were obtained by the heating of ethyl β,β' -dimethylglycidate with the corresponding amine in sealed tubes at 150-180°. It was shown experimentally that the addition of *p*-toluidine to the oxide ring occurs comparatively easily; a 6 hour heating at the above temperatures led to a 60% yield of ethyl hydroxy-*p*-toluidine-isovalerate. *o*-Toluidine added with much greater difficulty. Upon heating the reaction mixture for the same 6 hours, the reaction product was obtained only in a 26% yield. Apparently, such a low yield can be explained by steric hindrances caused by the methyl group of *o*-toluidine. The reaction time was increased to 30 hours and as a result, a 50% yield of ethyl hydroxy-*o*-toluidineisovalerate was obtained.

The position of the cleavage of the oxide ring in the glycidic acid chosen, as in the previous cases, was determined by location of the hydroxyl group in the molecule. It could be readily expected that both the isomeric toluidines in this case should behave similarly to aniline, i.e., would form the amino derivatives of α -hydroxyisovaleric acid.



Actually, both of the addition products obtained decarboxylated with the evolution of carbon dioxide by the action of concentrated sulfuric acid at 110-140°. This undoubtedly indicated that amino derivatives of α -hydroxyacids were being dealt with. For final solution of this problem, only the isolation of the decarboxylation products remained, which should be trimethyl indoles. This conclusion was possible on the basis of the investigated case of the decarboxylation of ethyl α -hydroxy- β -anilinoisovalerate where the product of the decarboxylation was 2,3-dimethylindole. Since in the given case toluidine, not aniline, was the starting material, the following must have been obtained: 2,3,5-trimethylindole from ethyl α -hydroxy- β -(*p*-toluidino)isovalerate, and 2,3,7-trimethylindole from ethyl α -hydroxy- β -(*o*-toluidino)isovalerate. The reaction of their formation can be described in the following manner on the example of 2,3,5-trimethylindole:



Indeed, upon making the acidic solution alkaline after the decarboxylation, the expected trimethylindoles were obtained which corresponded in analysis and melting point (individually and as the picrates) to the literature data. 2,3,5-Trimethylindole was isolated from the alkaline solution by steam distillation and was obtained in an 87% yield. 2,3,7-Trimethylindole was only distillable in small amounts with steam, and for this reason, it was extracted with ether from the alkaline solution; its yield was only 4% of the theoretical.

Such a great difference in the yields of the isomeric trimethylindoles, evidently, is explained by their different chemical stability. This difference, by the way, was apparent even during their storage. 2,3,5-Trimethylindole was stable, it only yellowed slightly upon 2-3 months standing in the air; 2,3,7-trimethylindole, on the other hand, darkened after a few days. Evidently, 2,3,7-trimethylindole is subjected more readily to the disruptive action of sulfuric acid than 2,3,5-trimethylindole; for this reason its yield was considerably smaller.

EXPERIMENTAL

Preparation of ethyl α -hydroxy- β -(*p*-toluidino)isovalerate. 13 g of *p*-toluidine and 20 g of ethyl β , β '-dimethylglycidate (the glycidic ester was used in excess in order to more completely use the *p*-toluidine) were sealed into a glass ampoule which was heated for 6 hours at 150-170°. The contents of the tube darkened slightly; there was no pressure when the tube was opened. The reaction mixture was vacuum distilled. The expected product distilled at 186-188° at 15 mm. It was a viscous straw-yellow liquid. Weight 17.8 g, which was 60% of the theoretical based on the *p*-toluidine. After one day, the substance crystallized; after recrystallization from aqueous alcohol, it melted at 54-55°.

0.0229 g substance: 1.12 ml N₂ (17°, 755 mm). 0.02105 g substance: 1.08 ml N₂ (18°, 755 mm).

Found %: N 5.3, 5.6; C₁₄H₂₁O₃N. Calculated %: N 5.57.

The conversion of ethyl α -hydroxy- β -(*p*-toluidino)isovalerate into 2,3,5-trimethylindole by the action of concentrated sulfuric acid. 2 g of ethyl α -hydroxy- β -(*p*-toluidino)isovalerate was added to 10 ml strong sulfuric acid. Upon heating the mixture on an open electric hot plate, the substance dissolved, and the evolution of carbon dioxide started at 110° (thermometer in the mixture).

The heating was continued to 140° until complete cessation of the formation of gas bubbles. The mixture assumed a dark red color. Then, without any initial cooling, the mixture was poured into cold water with ice. The acid was neutralized with sodium carbonate with the addition of some NaOH solution at the end to a clearly alkaline reaction. A white crystalline precipitate of 2,3,5-trimethylindole separated during the neutralization of the solution, which was steam distilled. 1.1 g of a colorless crystalline product with an unpleasant fecal odor was obtained. After recrystallization from dilute ethyl alcohol, the m.p. was 118-119°. The picrate, red-brown needles, m.p. 177-180°.

Found %: N 9.05. C₁₁H₁₃N. Calculated %: N 8.8. Literature data: melting point of 2,3,5-trimethylindole, 121.5°. Picrate, red brown needles, m.p. 177-180° [2].

Preparation of ethyl α -hydroxy- β -(*o*-toluidino)isovalerate. 15 g of ethyl β , β '-dimethylglycidate and 55 g of *o*-toluidine were sealed into a thick-walled tube and were heated for 30 hours at 170-180°. A slight pressure was present upon opening the tube. 15 g of a viscous straw-yellow liquid was isolated upon vacuum distillation. B.p. 134-135° at 2 mm. Yield 50 %.

d_4^{20} 1.0668; n_D^{20} 1.529. MR_D 71.23; Calculated 71.29.

0.2046 g substance: 12 ml N₂ (23°, 764 mm). 0.1805 g substance: 9.2 ml N₂ (23° 764 mm).

Found %: N 5.62, 5.74. C₁₄H₂₁O₃N. Calculated %: N 5.57.

Conversion of ethyl α -hydroxy- β -(*o*-toluidino)isovalerate into 2,3,7-trimethylindole by the action of concentrated sulfuric acid. 5 g of ethyl α -hydroxy- β -(*o*-toluidino)isovalerate was added to 15 ml of concentrated sulfuric acid in a small round-bottom flask. The mixture was heated in the same manner as in the previous experiment. The evolution of bubbles of carbon dioxide started at 110°. The heating was continued to 140° until the cessation of the evolution of carbon dioxide. The reaction mixture darkened strongly. The subsequent procedure was as in the previous case. The emulsion which separated in the alkaline solution was extracted with ether. After drying, the ether was removed, and the residue was vacuum distilled. B.p. 105-106° at 2 mm. The substance crystallized in the exit tube. 1.3 g was obtained, which was 41% of the original

yield. M.p. 86-87°. The picrate, red-brown crystals with m.p. 149-150°.

Found %: N 8.9, $C_{11}H_{13}N$. Calculated %: N 8.8.

Literature data: melting point of 2,3,7-trimethylindole, 75°. Picric acid, m.p. 155° [5].

SUMMARY

1. The reaction between ethyl 8,8'-dimethylglycidate and o- and p-toluidine was investigated. It was shown that the rupture of ring of the glycidic acid occurred at the site of the β -carbon atom by the action of both aromatic amines with the formation of nitrogen-substituted α -hydroxyisovaleric acids.

2. The conversion of ethyl α -hydroxy- β -(p-toluidino)isovalerate into 2,3,5-trimethylindole was accomplished; while 2,3,7-trimethylindole was obtained from ethyl α -hydroxy- β -(o-toluidino)isovalerate.

LITERATURE CITED

[1] See for example, O. V. Schickh, Ber., 69, 967 (1936); J. P. Billster, Bull. Soc. Chem., (5) 6, 1622 (1939); (5) 7, 593 (1940).

[2] "Dictionary of Organic Compounds" III, 862.

Received November 3, 1952

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Chair of the Theory of Structure of Organic
Compounds

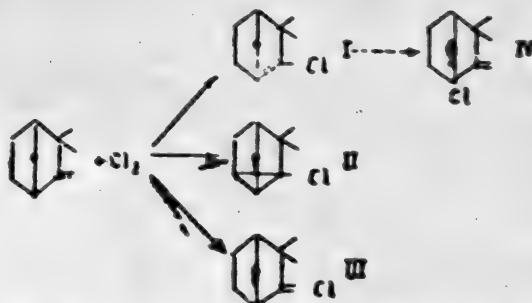


NEW TYPES OF TERPENE TRANSFORMATIONS

XIV. REACTION OF CHLORINE WITH CAMPHENE

D. Tishchenko

In communication I[1] general ideas were stated on the possible rules of the reaction of chlorine with terpenes, and predictions were given relative to the main direction of the reaction in each separate case and to the structure of the monochloroterpenes. For all cases studied up to now, without exception, these predictions were confirmed. They were also confirmed for the case of the reaction of chlorine with camphene. The sparse literature on the action of chlorine on camphene, reported in the same communication, gave no accurate description of the primary products of this reaction. For this reason, the prediction could only be proved experimentally. It was suggested that the "anomalous" reaction of M. D. Lvov must, for the case of camphene, be of less importance than for other terpenes, that camphene must be a "prohibited" system (Bredt's Rule), and that this reaction may proceed in three different directions.



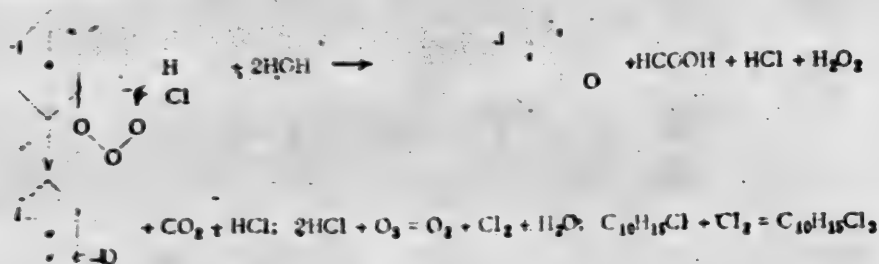
The degree of the "anomalous" reaction for camphene was found to be equal to 53-56% which is considerably lower than the corresponding value for other terpenes. Camphene monochloride is a mixture of the above three chlorides (I), (II) and (III). It is possible that chloride (IV) was present in small amounts in this mixture, but its presence was not proved beyond any doubt. The saturated camphene dichloride (product of the "classical reaction") was found to be a solid. Its structure did not follow the "rule of the smallest change in structure", which will be reported upon.

The mixture of monochlorides boiled within one degree. This fact alone indicated that the chlorine atom was structurally equivalent in all of these, and as it will be shown below, primary. As is known, secondary chloroterpenes boil 10-12° lower than the corresponding primary chlorides[2]. The investigation of this mixture posed very great difficulties, which were not unexpected. The structure of camphene proposed by Wagner, has been subject to doubts for more than thirty years because not even one transformation of camphene occurs uniformly, but always in different directions and is accompanied by isomerization. Even ozonolysis of camphene gives two products, camphenilone and a lactone. It was necessary to overcome the greatest difficulties during the investigation of the mixture of the three camphene monochlorides, to encounter many very unexpected results which did not have any analogy in chemical literature (see ozonolysis of one of the chlorocamphenes), and to study a series of transformations in order to come to a satisfactory conclusion by comparison of the results.

Initially, it was necessary to separate the mixture of chlorides, or the study of the transformations would have been senseless. The separation was accomplished by an exchange reaction with potassium acetate. The amount of active chlorine in the mixture of chlorides varied from 36-38% of the total. The chlorine at the double bond in chloride (III) must be inactive, the chlorine in chloride (II), a homolog of neopentyl chloride, must be only slightly

active. The chlorides with the inert chlorine, (II) and (III) were separated by this conversion from the camphene acetate, a derivative of chloride (I). It was necessary to assume that the structure of camphenol corresponded to that of chloride (I), which was confirmed: camphenol was found to be primary.

The ozonolysis of the chloride with the inactive chlorine consisting, as was finally shown, mainly of chloride (III) gave very surprising results. It was expected that camphenilone, hydrogen chloride, and formic acid would be obtained in equimolecular amounts.



Actually, only 30% of the theoretical yield of camphenilone was obtained upon ozonolysis of chloroform or acetic acid, and only 15% of hydrogen chloride. In addition to camphenilone, a widely boiling mixture of other products was obtained, which contained chlorine, from which a crystalline trichloride of composition $\text{C}_{10}\text{H}_{15}\text{Cl}_3$ could be isolated. This trichloride was readily volatile, and for this reason was mixed with all fractions boiling lower than camphenilone, and did not allow them to be obtained in pure form. A lactone was also present, which was detected by titration with hot alkali, but could not be isolated pure. The same amounts of camphenilone and trichloride were also obtained upon ozonolysis of the inert chlorocamphenes in a mixture of glacial acetic acid and acetic anhydride, followed by decomposition of the ozonide by heating the solution to boiling, removing the solvents, and distilling the residue. This shows that the formation of the trichloride is not due to the cleavage of the ozonide by water, and occurs at the time of the ozonolysis. It can be suggested that the ozonide splits into camphenilone, carbon dioxide, and hydrogen chloride; the latter is partially oxidized by ozone to chlorine, which then adds to chloride (II) to form the trichloride $\text{C}_{10}\text{H}_{15}\text{Cl}_3$. The aqueous solution from the cleavage of the ozonide with water gave a qualitative reaction for formaldehyde, and a small amount of dimedone formal could be obtained from it. One of the higher boiling fractions contains the trichloride and a substance of the composition $\text{C}_9\text{H}_{13}\text{OCl}$. These two facts are proof of the possibility of the presence of chloride (IV) in the mixture of inert chlorides. At first glance, the chlorine in chloride (IV) appears strange (tertiary chlorides of the allylic type), but the chlorine is found at the carbon atom which stands at the head of a triple bridge. For this reason, any exchange reaction of the chlorine, occurring usually with a Walden inversion, is only possible in the case of the rupture of one of the bridge carbon atoms, which requires a very high energy of activation. Examples of the inertness of such tertiary chlorides are known [3]. Since only camphenilone, isolated in only 30% of the possible quantity, is an undoubted derivative of chloride (III), and the formation of the trichloride of unknown structure cannot be assigned to any known chlorocamphene, it was necessary to recognize that the method of ozonolysis did not prove the theory in the given case, because of the unexpected side reactions, and that it was necessary to search for some other transformation giving more definite products in better yield.

Similar results were given by the method of preparing oxides from a mixture of inert chlorides by the action of benzoyl hydroperoxide in chloroform solution.

Part of the chlorides did not react (actually chloride (II)): a crystalline substance of composition $\text{C}_{10}\text{H}_{15}\text{OCl}$ was obtained in about 35% yield based on the reacted chloride. In addition, a complex mixture of high boiling products was obtained in the same yield as the camphenilone, and was a substance of unestablished structure; further study of this transformation and its products was not made.



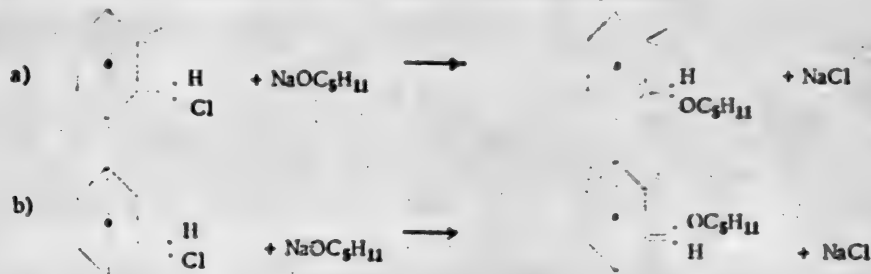
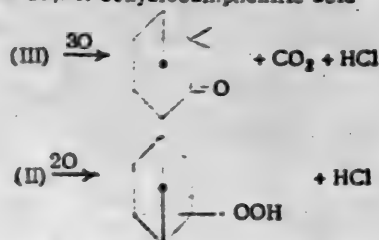
An attempt to obtain primary oxidation products from the mixture of inert camphene chlorides by an insufficient amount of potassium permanganate in aqueous suspension, or in acetone solution was also unsuccessful. In spite of great variations in experimental conditions, the main part of the chlorides was recovered, while the oxidized part appeared as a mixture of extensively oxidized products which did not allow a clear-cut conclusion on the contents of any chlorocamphenes in the starting mixture. For this reason, the corresponding experiments are not reported in the experimental section.

The best results were given by the oxidation of the inert chloride in 80% acetic acid by an excess of dry

potassium permanganate. About 60% of the possible yield of camphenilone and 10% of dehydrocamphenilic acid were obtained with a consumption of about 10 g-atoms of active oxygen.

The products obtained require a very much smaller oxygen consumption. For this reason it must be recognized that there is another chloride in the mixture in addition to chlorides (III) (camphenilone is not oxidized by permanganate), and (II), which is oxidized much more extensively, or that part of dehydrocamphenilic acid was subjected to more extensive oxidation.

The same results on the amount of chloride (III) in the mixture were obtained by the study of the action of sodium amylate in isoamyl alcohol on the inert chlorocamphenes. Upon boiling the chlorides with sodium isoamylate in isoamyl alcohol, 67% of the chlorine was mineralized after 23 hours, and the reaction then stopped. 31% of the starting chloride, and 44%, based on the chloride reacted, of the isoamyl enol ether of camphenilanic aldehyde were found in the reaction products.



The ether gave upon hydrolysis with 3% hydrochloric acid, isoamyl alcohol and camphenilanic aldehyde, which was oxidized to isocamphenilanic acid with m.p. 117° by permanganate.

A semicarbazone was obtained from camphenilanic aldehyde which melted at 192-193° after two recrystallizations from alcohol. Henderson [4] gives an m. p. 191-192°. However, these results are untrue. Continued recrystallization of the above preparation from alcohol-benzene raised it to 207-208° after 4 recrystallizations; it did not change upon subsequent recrystallization from other solvents.

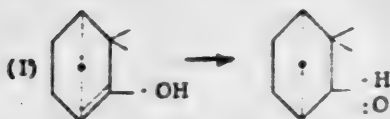
The chlorocamphene recovered from heating with sodium isoamylate was ozonized. Camphenilone was obtained in about 30% of the possible yield. This fact can be explained because chloride (III) was a mixture of *cis* and *trans* forms a and b of which form a reacts with sodium isoamylate at lower temperatures (absence of steric hindrance from the side of the gem dimethyl group), than form b. In this case, the recovered chloride (form b) must react with sodium isoamylate at higher temperatures, which was confirmed experimentally. 70% of the chloride reacted in 5 hours at 210° in a sealed tube. 50% of the isoamyl camphenilic ether, based on the chloride reacted, was obtained. The total yield of the ether from forms a and b was slightly more than 60%. Therefore, the mixture of inert chlorides contains not less than 60% of chloride (III), which agreed with the results of the oxidation.

The presence of chloride (II) in the mixture was established by another method. It was stated above that, during the oxidation of the inert camphene chloride by a permanganate solution, the main part of the chloride was recovered. It was oxidized many times until the chloride began to be oxidized very slowly by permanganate solution. This chloride was converted into an organosodium compound by treatment with powdered sodium in isopentane, and was decomposed with water. The hydrocarbon obtained (b. p. 151-154°) melted at 36-42°, it was purified from contaminants by Lipp's method [5]; it then melted at 58-68°. Camphene melts at 50°; tricyclene at 68°.

The structure of the chlorocamphene with the active chlorine, as stated above, had to be determined by means of the camphenol obtained from it, since the mixture of chlorides boiled within 1° and could not be separated by physical methods. Chlorides (II) and (III) were primary; for this reason, it could be assumed that chloride (I) was primary, and the chlorine atom in it bound to the same carbon atom in the isocamphene skeleton as in chlorides (II) and (III). Its acetate, obtained by the reaction with potassium acetate with the initial mixture of chlorides, boiled within 1°, its molecular refractivity, MRD (54.89) was somewhat greater than that calculated for the formula $\text{C}_{10}\text{H}_{15}\text{OCOCH}_3$ (54.40). The ester was completely saponified only after a 6 hour boiling with alcoholic alkali which agreed with the structure (I) (sterically hindered). The alcohol obtained by the saponification of the ester was solid and homogenous, melted at 59-60°; it formed an acid phthalate melting at 142-143° on boiling with phthalic anhydride in benzene; therefore, the alcohol was primary. This fact leads to the conclusion that its structure corresponds to that of chloride (I) (primary). The acid phthalate was not obtained quantitatively by the

reaction of equimolecular amounts of the alcohol and phthalic anhydride in boiling benzene. Simultaneously there was obtained a diphthalate, resulting in the formation of water which hydrolyzed the phthalic anhydride to the acid, and a certain part of the alcohol isomerized into an aldehyde (or mixture of aldehydes). Upon the deliberate addition of water to the reaction mixture, the aldehyde could be obtained in considerable yield. Its semicarbazone could be

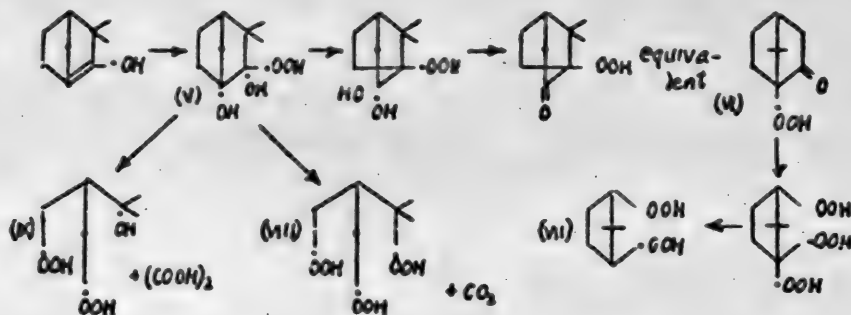
separated into poorly and readily soluble parts by crystallization from alcohol. The first part was brought to a constant m.p. 205-207° by recrystallization from alcoholic-benzene. A mixed melting point with camphenilanic aldehyde semicarbazone (see above) gave no depression. The readily soluble part was brought to a m.p. 148-149° by recrystallization from benzene. It was not determined to what aldehyde the last semicarbazone corresponded. The isomerization of the alcohol is in complete



agreement with structure (I') and is analogous to that of allylic alcohol to propionaldehyde.

Structure (I) and (I') do not follow Bredt's rule, but this rule is not a law and exceptions to it are known [6]. In alcohol (I'), the double bond is found in the ring; for this reason, the careful oxidation of any of its esters with subsequent saponification must result in the neutral substance of composition $C_{10}H_{16}O_3$, which does not show an aldehydic reaction. By the oxidation of the sodium salt of the acid phthalate of the above alcohol with aqueous permanganate (2 gram atoms of oxygen), this substance was obtained in a yield of 40% of the possible, which confirmed the presence of a cyclic double bond in this alcohol.

A more extensive oxidation of alcohol (I') can be described by the following scheme if the experimentally established oxidation course of camphene [7] is kept in mind:



In this diagram, oxidation of the alcohol (I') accompanied by an intermediate pinacolin rearrangement, yields ketopinic acid (VI) and cis-apocamphoric acid (VII), while without the rearrangement it yields isocamphoric acid (VIII), a hydroxydicarboxylic acid (IX), and exalic acid. Oxidizing isocamphenol in aqueous solution with an excess of potassium permanganate yielded cis-apocamphoric acid and its anhydride, isocamphoronic acid, oxalic acid, and acetic acid. About one-third of a mole of acetic acid was recovered per mole of camphenol. When camphenol was oxidized with a lesser quantity of permanganate, we got ketopinic acid. These experimental findings fully agreed with the suggested scheme for the oxidation of camphenol, which enables us to adopt the structure (I') for it with adequate certainty. What was unexpected was the securing of a small quantity of acetic acid, which is not oxidizable by permanganate, as we know. Its formation may be explained by the dehydration of the hydroxy isopropyl group of the unseparated acid (IX) to an isopropenyl group followed by the latter's oxidation. We were wholly unable to confirm this hypothesis, however.

The camphenol (I') is extremely easily soluble in all organic solvents, which made it difficult to recrystallize it to secure a constant melting point (59-60°). This was accomplished from aqueous methanol chilled to -20°. When we tried to recrystallize it from 70% acetic acid, in which it is moderately soluble, we found that the melting point rose with each successive crystallization, finally coming to a stop at 176-178°. A sample of camphenol with a m.p. of 59-60°, kept for 2 years in a not-tightly-sealed bottle in a draft where strong acids were present, exhibited a broad melting range (about 120-140°); recrystallizing it from acetic acid yielded crystals with a m.p. of 176-178°, which smelled of camphor and "skittered" over the surface of the water like camphor. A sample of these two specimens, mixed with inactive camphor (m.p. 176-178°) exhibited no depression of the melting

point, so that they may be regarded as camphor. The isomerization of camphenol to camphor may be represented as follows, if we adopt its structure as (I'):



Therefore, the action of comparatively weak acids in low concentration isomerizes camphenol (I') into camphenilanic aldehyde, it is transformed into camphor by the action of comparatively weak acids in high concentration, or strong acids at low concentration.

EXPERIMENTAL

Chlorination of Camphene

The chlorination of camphene was conducted under previously (see previous communication) reported conditions with the only difference being that carbon tetrachloride was added in an amount necessary for the solution of the camphene. Isomerized camphene, filtered at 30-35° with m.p. 47-49°, was used. A report of one of these experiments is given below.

Camphene 350 g, CCl_4 150 g, NaHCO_3 200 g, KMnO_4 100 g, HCl (1.19) 750 ml. The chlorine in the chlorides after the removal of the CCl_4 and part of the camphene, 78.9 g, in salts, 31.1 g; yield of the "anomalous" reaction, 56%.

The CCl_4 and part of camphene were removed in water pump vacuum, the remaining camphene and the monochlorides were distilled through a herringbone, of 4-5 plates at 2 mm. Used initially: camphene 350 g, chlorine 110 g, total 460 g. Obtained: camphene 126 g, fraction 60-61° 128 g, crystalline residue 130 g, chloride ion 31 g, total 415 g; loss (camphene) 45 g.

Fraction 60-61° at 2 mm; d_4^{20} 1.009; n_D^{20} 1.4944.

Found %: Cl 20.4, 20.3. $\text{C}_{10}\text{H}_{15}\text{Cl}$. Calculated %: Cl 20.7.

The amount of active chlorine was determined by a 4 hour boiling with potassium acetate in acetic acid, and was equal to 36.5% of the total amount of chlorine.

The crystalline part was recrystallized from alcohol until the melting point remained unchanged at 134.5-135°. The substance was readily soluble in gasoline, benzene, acetone, ether, less in cold alcohol. It did not react with bromine water or permanganate solution.

Found %: Cl 34.5, 34.4. $\text{C}_{10}\text{H}_{15}\text{Cl}_2$. Calculated %: Cl 34.3.

Separation of the Monochlorides

330 g of monochlorides containing 35.0% of active chlorine of the total amount was heated to boiling in 500 ml of acetic acid with 200 g of potassium acetate for 8 hours. 53 g of KCl precipitated; the reaction had occurred completely. The acetic acid was distilled through a branched column in a water pump vacuum, the residue was diluted to 1 liter with water, extracted with ether, the ether was removed from the extracts, the residue distilled through an 8-10 plate column at 1 mm. These fractions were obtained: 1) up to 53°-5 g, 2) 53-64°-204 g, 3) 54-73°-5 g, 4) 73-74°-87 g, 5) 73-190°-10 g, residue 5 g, loss 28 g (in acetic acid).

Fraction 2: d_4^{20} 1.018; n_D^{20} 1.49245; MR_D 48.65; calculated 48.38.

Found %: Cl 20.6, 20.7, weight of bound chlorine. $\text{C}_{10}\text{H}_{15}\text{Cl}$. Calculated %: Cl 20.7.

Fraction 4: d_4^{20} 0.991; n_D^{20} 1.4731; MR_D 54.89; calculated 54.40.

Found saponification No. 284, 286. $\text{C}_{10}\text{H}_{15}\text{OCOCH}_2\text{F}$. Calculated saponification No. 288.

Ozonolysis of Inert Monochlorides

5% by weight of ozone was passed into a solution of 34 g of the chloride in 100 ml of chloroform until saturation of the double bond. The ozonide solution was dropped into boiling water, the volatiles were steam distilled, the chloroform layer was distilled separately; the chloroform was removed and the residue (29.5 g) was distilled at 3 mm through a 6-6 plate column. The following fractions were obtained 1) to 56°-1.3 g, 2) 56-57°-9.0 g, 3) 58-80°-2.8 g, 4) 80-106°-4.0 g, 5) 106-130°-10.0 g, residue 2.0 g.

Fraction 2: d_4^{20} 0.998; n_D^{20} 1.4785. Found %: Cl 6.1 and 6.3.

The fraction solidified at -20° , the crystals were filtered and dried on a porous plate; m.p. $36-37^\circ$; camphoric odor.

Found %: C 77.9; H 10.1. $C_9H_{14}O$. Calculated %: C 78.2; H 10.1.

The substance was camphenilone. An oxime was prepared which was recrystallized to a constant m.p. $105-105.5^\circ$ corresponding to camphenilone oxime.*

Fractions 3 and 4 were combined and distilled through a micro column. 1.8 g of a fraction with b.p. $70-72^\circ$ at 1.5 mm was obtained; d_4^{20} 1.105.

Found %: C 63.0, 63.3; H 7.7, 7.9; Cl 20.1, 20.0. $C_9H_{13}OCl$. Calculated %: C 62.8; H 7.5. Cl 10.5.

In other experiments on the ozonolysis, this fraction of the chloroketone could not be isolated in such pure form; it contained more chlorine, less carbon, but if it was assumed that the fraction consisted of the chloroketone, and the trichloride $C_9H_9Cl_3$, and the amount of trichloride was calculated by means of the excess chlorine content, a satisfactory agreement of the analytical data with the calculated was obtained.

Fraction 5 was titrated with normal alkali while heated on the boiling water bath (it did not titrate in the cold, lactone type of neutralization). The insoluble part semisolidified on cooling. The crystals were filtered (1.8 g) and recrystallized from alcohol until a constant m.p. $127-128^\circ$ was obtained. The substance did not react with bromine and permanganate solutions.

Found %: Cl 44.2, 44.6. $C_{19}H_{15}Cl_7$. Calculated %: Cl 44.2.

Amount of chlorine initially in fraction 5: Found 26.7-26.5%.

In the water in the distillation flask and the aqueous layer formaldehyde was detected qualitatively (fuchsine sulfurous acid + 0.1 N HCl, preparation of formal dimidone with m.p. $186-189^\circ$), and 0.968 g Cl⁻ was found, i.e. 13.6% of the total amount. The yield of camphenilone was about 21%.

32 - 35% of camphenilone could be obtained in other ozonolysis experiments in solutions in acetic acid and acetic anhydride, but the yield of hydrogen chloride was always about half. The trichloride was always obtained.

Preparation of Chlorocamphene Oxide

40 g of chlorides, 28 g of benzoyl hydroperoxide, 800 ml of chloroform. Parallel blank experiment. End of reaction after 72 hours. The acids in solution were neutralized with dilute alkali, the chloroform removed, the residue (37.5 g) distilled at 3 mm through a 6-8 plate column. The following fractions were obtained: 1) $64-65^\circ$ - 14 g, 2) $65-85^\circ$ - 2 g, 3) $85-90^\circ$ - 11 g (fraction crystallized), 4) $90-120^\circ$ - 2 g, 5) $120-180^\circ$ - 3 g, residue 1.3 g.

Fraction 3: Found %: Cl 18.9, 18.9. $C_{13}H_{15}OCl$. Calculated %: Cl 12.0.

The crystals were pressed on paper; m.p. $90-110^\circ$; they half melted in an open beaker with the evolution of HCl within 24 hours.

Oxidation of the Inert Camphene Chlorides

105 g of $KMnO_4$ was added stepwise with stirring to 40 g of the chloride in 400 ml of acetic acid and 100 ml of water; it heated spontaneously to boiling. After filtration, the light rose solution was steam distilled until the distillate no longer clouded upon dilution with water. The distillate was extracted three times with equal volumes of light gasoline ($20-40^\circ$), the gasoline was removed from the extracts, and the residue (13.8 g) was distilled through a microcolumn at 23 mm. The following fractions were obtained 1) to 86° - 0.5 g, 2) $86-90^\circ$ - 9.5 g, 3) $90-130^\circ$ - 0.5 g, 4) $130-150^\circ$ - 1.5 g, residue 0.5 g.

Fraction 2 solidified completely in the receiver; m.p. $36-37^\circ$. The oxime prepared from it melted at $105-106^\circ$ after the first recrystallization from alcohol. The melting point did not change upon subsequent recrystallization. The substance was camphenilone.

Fraction 4 and the residue also crystallized. The crystals were pressed on a porous plate and recrystallized from aqueous alcohol to a constant m.p. $150-151^\circ$. The gram equivalent found was 166. The acid was dehydro-

* Literature references are not given if the data are given in Beilstein's Handbook.

camphenilic.

Reaction of Sodium Isoamylate with the Inert Chlorocamphene.

87 g of the chloride was heated to boiling with a solution of 16 g of sodium in 250 ml of isoamyl alcohol. NaCl separated and the alkalinity of the solution decreased gradually (titration of an aliquot with acid); after 23 hours the reaction ended; the alkalinity did not decrease any more. According to the alkali consumption, 67% of chlorine was mineralized. The reaction product and the amyl alcohol were steam distilled until no more of an oil came over. 0.347g-equiv. of mineralized chlorine was found in the distillation flask; the same as by consumption of alkali. The amyl alcohol layer was distilled through a 6-8 plate column at 6 mm. After the removal of the alcohol, the following were obtained: 1) 73-75°-31.3 g, 2) 75-90°-2.0 g, 3) 90-92°-8.2 g, 4) 92-123°-2.7 g, 5) 123-125°-33.8 g, residue 6.1 g.

Fraction 1 (d_4^{20} 0.996; Cl % 19.6 and 19.4) was camphene chloride.

Fraction 5 d_4^{20} 0.917; n_D^{20} 1.4800.

Found %: C 80.4, 80.6; H 11.8, 11.8. $C_{10}H_{16}O$. Calculated %: C 81.03, H 11.7.

15 g of the fraction and 300 ml of 3% HCl were distilled from a flask through a branched column until no more oil distilled. The distillate was extracted with ether, the ether was removed from the extracts, and the residue (14.0 g) distilled: 1) 126-132°-3.0 g, 2) to 79° at 6 mm-0.8 g, 3) 79-82°-5.5 g, 4) 82-130°-4.2 g, residue 1.2 g.

Fraction 1: d_4^{20} 0.816; n_D^{20} 1.4124 had the odor of isoamyl alcohol.

Fraction 3 solidified in the receiver; the crystals, pressed on a plate, melted at 65-69° (camphenilanic aldehyde melts at 68-70°). A semicarbazone was obtained from these which was taken to a m.p. 207-208° (See above). 1 g of the crystals was oxidized with aqueous permanganate. The acid obtained melted at 108-112° without recrystallization; after the first and second recrystallization from hot water, the m.p. was 117° as necessary for isocamphenilanic acid.

Found: g-equiv. 169; % C 71.5; H 9.8. $C_{10}H_{16}O_2$. Calculated: g-equiv., 168; % C 71.4; H 9.5.

The chlorocamphene which did not react with sodium amylate, was ozonized. 32% of crystalline camphenilone with m.p. 35-37° was obtained; m.p. of the oxime, 106-106.5°.

30 g of the same chlorocamphene was sealed into two tubes with a solution of 4.6 g of sodium in 100 ml of isoamyl alcohol and was heated for 5 hours at 205-210°. The contents of the tubes was poured into water, 4.12 g of chloride ion was found in it corresponding to 70% of the chlorine in the chlorides. The oily layer was distilled at 12 mm. 14.3 g of a fraction 128-131° was obtained: d_4^{20} 0.916; n_D^{20} 1.4729. 12 g of the fraction was distilled with 300 ml of 3% of hydrochloric acid. The following were obtained: isoamyl alcohol, and camphenilanic aldehyde with m.p. 63-67°, which was oxidized to isocamphenilanic acid with m.p. 117°.

Preparation of Tricyclene from the Inert Camphene Chloride

14.4 g of the chloride recovered from several subsequent experiments with insufficient amounts of permanganate (not reported), were dropped with stirring onto 14 g of powdered sodium covered with isopentane. A spontaneous evolution of heat occurred, and the solvent boiled. Upon cooling, the solution of the organo-sodium compound was poured from the excess sodium and NaCl, and decomposed with water. The pentane layer was separated and distilled. 3.8 g of a solid hydrocarbon with b.p. 151-154° and m.p. 36-42° was obtained. The substance was oxidized with permanganate in acetic acid to a stable rose color, steam distilled, the crystals on the distillate were pressed on a paper (very volatile), dried over potassium hydroxide. M.p. 58-68° which corresponded to somewhat impure tricyclene.

Saponification of Camphenol Acetate

110 g of the ester (for constants see above) was saponified by a 6 hour boiling with 60 g of KOH in 200 ml of alcohol, the solution diluted with three volumes of water, and extracted with isopentane. The solvent was removed from the extract, the residue distilled at 11 mm. 80 g of a solid camphenol, b.p. 104-105° and m.p. 43-56° was obtained. It was very readily soluble in the usual solvents. It was recrystallized from 80% methanol with cooling to -20° until a constant m.p. of 59.5-60°. With less saponification time, the alcohol was obtained as a liquid because of impurities of the ester. It was recrystallized from alcohol and analyzed.

Found %: C 79.1, 79.0; H 10.5, 10.7; OH (Chugaev-Tserevitinov) 11.7, 11.2. $C_{10}H_{16}O$. Calculated %: C 78.9; H 10.4; OH 11.2.

Preparation of Camphenol Acid Phthalate

66 g of camphenol with m.p. 43-56°, 66 g of freshly sublimed phthalic anhydride, and 300 ml dry benzene were

heated to boiling for 2 hours. Water droplets collected from time to time in the condenser and were removed by wiping with filter paper. After the solution cooled, 25 g of phthalic anhydride crystals (g-equiv. found 67.6) precipitated. The benzene was removed, and the residue was dissolved in 300 ml of gasoline with heating (70-100°). Upon cooling to -23°, 55 g of the acid phthalate with m.p. 137-141° came out. The solvent was removed from the mother liquor through a column on the boiling water bath, using a water pump vacuum, and the residue was dissolved in 100 ml of gasoline. 12 g more of the phthalate with m.p. 135-139° came out at -23°. The gasoline was removed from the solution, and 1 g of a mobile liquid giving an aldehyde reaction was distilled from the substance on the water bath at 0.02 mm and up to 60°, and at 60-62° 18.7 g of camphenol melting at 46-52°, without recrystallization. Weight of the residue, 21.5 g; it was dissolved in 100 ml of hot gasoline. The gasoline was removed in vacuum from the mother liquor; weight of the final residue, 14.0 g (see below). Weight of products, 133.5 g; no losses. 16 g of recovered camphenol was heated for 15 hours to boiling with 16 g of phthalic anhydride. The benzene was completely removed in vacuum at the end. The residue was dissolved in 200 ml of boiling gasoline, and 2.0 g of phthalic anhydride was filtered off (g-equiv. 83.6). Upon cooling of the solution, 24 g of an acid phthalate with m.p. 135-138° came out. All four residues were recrystallized from gasoline with very small losses to constant melting point, alone and in mixtures, of 142-143°. Light, fluffy needles which caused violent sneezing upon entering the nose. G-equiv. found 301. Calculated for $C_{15}H_{15}-OOC-C_6H_4-COOH$ 300. Camphenol was homogeneous and primary [8].

The usual method for the isolation of the phthalate from the benzene solution did not apply in this case. Upon treatment of the solution with sodium carbonate, a colloidal, opalescent solution of benzene in the aqueous solution of the sodium salt of the phthalate was obtained. This phenomenon is known under the name of "hydrotropy", and is mentioned for many salts of organic acids.

14 g of the final residue was dissolved in ether, and treated with an excess of sodium hydroxide solution; 2 g dissolved. The ether was removed; weight of the neutral viscous substance, 12.0 g. It distilled almost completely at 146° and 0.08 mm. The saponification of 10 g of this fraction with alcoholic alkali gave 3.5 g of phthalic acid, isolated in the form of the potassium salt which was difficultly soluble in alcohol, and 6.0 g of camphenol with b.p. 100-101° at 9 mm and m.p. 46-54° (without recrystallization). An acid phthalate was obtained from the camphenol with m.p. 142-143° alone and mixed with the previous samples.

Isomerization of Camphenol into the Aldehyde

In one experiment on the preparation of camphenol acid phthalate from 69 g of the alcohol, 2-3 ml of water fell into the reaction flask because of a poorly fitted reflux condenser. The contents of the flask were heated to boiling for 12 hours. Upon cooling, 16 g of phthalic acid crystallized. The benzene solution was distilled. The residue did not crystallize upon the removal of the benzene; it was a mobile liquid with a strong individual odor different from that of camphenol, resembling that of camphor. It was distilled through a 6-8 plate column at 17 mm. 36 g of a fraction with b.p. 88-89° was obtained.

d_4^{24} 0.9525; n_D^{21} 1.4676; M_{10}^D (for aldehyde $C_{15}H_{15}O$) found 44.33; calculated 44.0.

The substance gave all of the qualitative tests for aldehydes. 6 g of the fraction was heated for 1 hour to boiling with 4.5 g of semicarbazide acetate in 50 ml of alcohol, half of the alcohol was distilled off, and the residue diluted with four times as much water. A solid precipitated which was separated by means of alcohol into difficultly (2.2 g) and very readily (2.0 g) soluble parts. Recrystallization of the first part from alcoholic benzene, and the second from benzene, led to constant m.p.'s of 205-207°, and 148-149°, respectively. The first semicarbazone melted without depression when mixed with solid camphenilanic aldehyde semicarbazone (m.p. 207-208°). See the general section for the isomerization of camphenol into camphor.

Oxidation of Camphenol Acid Phthalate in the Neutral Substance $C_{15}H_{15}O_2$

13.5 g of the phthalate was dissolved in 300 ml of water and 5 g of $NaHCO_3$ and 10 g of $KMnO_4$ in 500 ml of water was added dropwise with cooling and stirring to the solution; the MnO_2 was filtered, the filtrate was acidified, and extracted with ether. The ether was removed from the extracts; weight of the residue, 15.2 g; it was saponified by a 2 hour boiling with 110 ml of normal alkali. The water was removed in vacuum from the solution, and the solid residue was extracted 4 times with 100 ml of acetone with rubbing. The acetone was removed from the extracts; weight of the semi-solid residue, 4.6 g. It did not distill, but sublimed at 0.1 mm; 3.5 g of a solid sublimate was obtained in a sabre flask and 0.9 g of a residue. The sublimate was recrystallized from benzene; fine, dense crystals with m.p. 169-170°

Found %: C 65.3, 65.5; H 8.9, 8.8. $C_{15}H_{15}O_2$. Calculated %: C 65.3; H 8.7.

The substance did not give an aldehyde reaction; it evidently was a diketoalcohol.

Oxidation of camphenol leading to ketopinic acid

1400 ml of a 4% permanganate solution was added with stirring and heating to 75° on a bath, to 10 g of camphenol suspended in 100 ml of water. The manganese dioxide was filtered, leached twice with 1/2 liter of boiling water, the combined filtrates evaporated to 50 ml, and acidified to Congo with hydrochloric acid, d 1.10. The precipitated potassium chloride was filtered, and washed with ether; the filtrate was extracted four times with ether, and the ether removed from the extracts; weight of the viscous residue, 11 g. It was dissolved in alcohol, and four volumes of benzene were added to the solution; 0.55 g of crystals deposited. They were recrystallized from hot water; clusters of thin prisms; m.p. 230-232°.

Found %: C 65.2; H 7.6; g-equiv. 186. $C_{15}H_{14}O_3$ (ketopinic acid). Calculated %: C 65.9; H 7.4; g-equiv. 182. Ketopinic acid melts at 233.5-234.5°.

Extensive oxidation of camphenol

32 g of camphenol in a liter of water (flask with reflux condenser and stirrer) was oxidized with stirring and heating (toward the end at 75°) with dry permanganate added slowly until a stable rose color (180 g). The manganese dioxide was filtered, leached four times with a liter of boiling water, the combined filtrates distilled to 300 ml, the distillate and residue extracted four times with ether, and the ether removed from the extracts; weight of the residue (neutral substances), 0.6 g; it was not investigated. The alkaline residue (300 ml) was acidified to Congo with hydrochloric acid, and the carbon dioxide collected in a gasometer (3950 ml). The acidic solution was steam distilled to a neutral distillate; amount of volatile acids, calculated as acetic, 4.07 g. The distillate was neutralized with sodium hydroxide, evaporated, the salt fused, weight, 5.7 g; 5.7 g of sodium acetate was expected. Part of the salt was converted to the silver salt; its silver content amounted to 64.6%, corresponding to that of acetic acid. One tenth of the acid solution from the distilling flask was saturated with an excess of calcium chloride, the precipitate was filtered, washed, and dried at 170°; wt. 0.170 g. Found %: CaO 43.6. C_2O_4Ca . Calculated %: CaO 43.7.

The remaining acid solution was extracted three times with equal volumes of ether, the ether was removed from the extracts; weight of the viscous residue, 14 g (acid I). The aqueous layer was evaporated until the start of salt crystallization; it was filtered, washed with a small amount of cold water, the combined filtrates extracted three times with ether, and the ether removed from the extracts; weight of the viscous residue, 5.3 g (acid II). The aqueous layer was slowly evaporated along with the filtered mineral salts; weight of the viscous residue, 11.0 g; it was insoluble in acetone; upon combustion, an alkali salt remained. 5 ml of fuming hydrochloric acid was added to it, and the reaction product was extracted with ether 3 hours later. 7.3 g (acid III) was extracted.

Acid I did not crystallize after 3 weeks. 6.4 g of a substance was sublimed from a saber flask at a bath temperature of 160-160° and 1.10×10^{-4} mm; weight of the residue, 5.7 g; loss 2.5 g. The sublimate was dissolved in acetone, benzene was added dropwise to it until a cloudiness formed. 1.2 g of crystals deposited; they were recrystallized to a constant m.p. 208-209° (small cubes).

Found %: C 58.3; H 7.8; g-equiv. 93.5. $C_9H_{14}O_4$ (Cis-apocamphoric acid, m.p. 206-208°).
Calculated %: C 58.1; H 7.5; g-equiv. 93.0.

The acetone-benzene mother liquor was evaporated to dryness, the residue dissolved in gasoline, and poured in a crystallizer. Growths of needles surrounded by an oil appeared as the gasoline evaporated. They were pressed on paper and recrystallized from gasoline to an m.p. 175-176°. The substance was not titrated by alkalis in the cold; it could be titrated while boiling; g-equiv. 84.8 g. Cis-apocamphoric acid anhydride melts at 176°, g-equiv. 84. The substance was dissolved in alkali, the solution was acidified to Congo with hydrochloric acid, and poured into a crystallizer. Four days later, cubes of cis-apocamphoric acid with m.p. 208-209° and g-equiv. 93.3 were obtained.

Acid II solidified after 60 days into a slurry of crystals surrounded by a viscous liquid. They were spread on a porous plate and placed into a desiccator with 10 ml of ether. A white powder remained on the plate (3.2 g) with m.p. 160-172° and g-equiv. 72.3. It was recrystallized to a constant m.p. 166-167°.

Found %: C 49.2; H 6.5; g-equiv. 72.6. $C_9H_{14}O_6$ (isocamphoric acid, m.p. 166-167°). Calculated %: C 49.5; H 6.4; g-equiv. 72.7.

Acid III did not crystallize in 90 days. It was dissolved in ether, gasoline was added, the solution poured into a crystallizer. Crystals surrounded by an oil appeared as the gasoline evaporated. The crystals, 2.2 g, were filtered, dissolved in 10 ml of water, and allowed to stand in an open beaker. Two weeks later, crystals deposited. M.p. 164-166°, g-equiv. found 71.1 — isocamphoric acid.

SUMMARY

1. The action of chlorine on camphene was studied. In contrast to all other terpenes, three monochlorides were formed as primary products: ω -chlorocamphene (III), 7-chlorotricyclene (II) and bicyclo [1,2,2]-3-chloro-2-methyl-2,2-dimethylheptene-3 (I); the latter was formed in opposition to Bredt's rule. The possibility of the formation of these chlorides was suggested in communication I.

2. The extent of the "anomalous" reaction was lower than with other terpenes ($\sim 55\%$); saturated dichlorocamphene was formed in a yield of about 40%.

3. The following were obtained by ozonolysis of chloride III, independent of the conditions of ozonolysis and decomposition of the ozonide: campherilone ($\sim 30\%$), hydrogen chloride ($\sim 15\%$), and a saturated trichloride $C_{10}H_{15}Cl_3$. There is no analogy in the literature for the formation of the trichloride.

4. Chloride (I) was almost quantitatively saponified (via the acetate) into the corresponding terpenol (I'). The latter could be isomerized into camphenilanic aldehyde, as well as into camphor.

5. Chloride (III) was a mixture of cis and trans forms reacting at various temperatures with sodium amylate to form the amyl enol ether of camphenilanic aldehyde. Camphenilanic aldehyde semicarbazone had m.p. 206-207°, and not 191-192° [4].

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Received June 20, 1962

The S. M. Kirov Forest Technology
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* See Consultants Bureau Translation, page. 593.

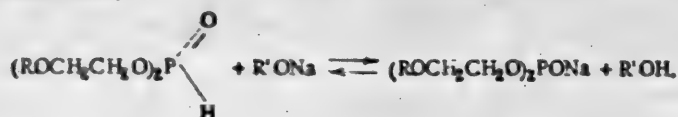
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REACTION OF DIALKYLPHOSPHORIC ACIDS WITH ALDEHYDES AND KETONES

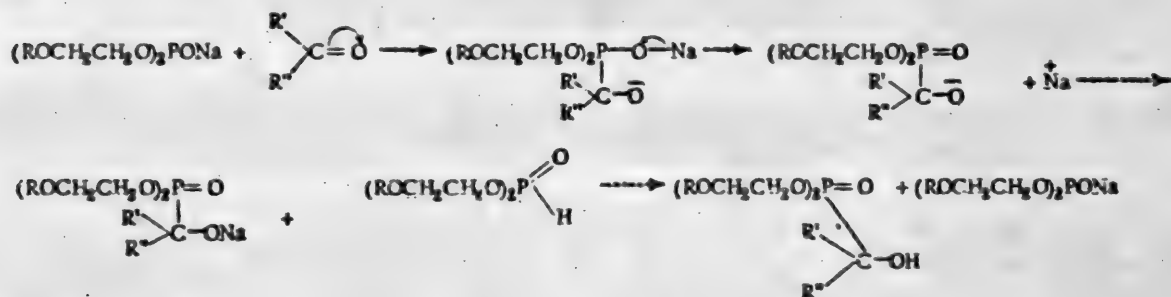
V. β -METHOXYETHYL AND β -ETHOXYETHYL ESTERS OF α -HYDROXYALKYLPHOSPHINIC ACIDS

V. S. Abramov, Yu. A. Bochkova, and A. D. Polyakova

In the previous communications [1] it was shown that dialkylphosphoric acids reacted with aldehydes and ketones. The reaction occurs in the presence of freshly prepared alkali metal alcoholates. The methyl, ethyl, propyl, and other α -hydroxyalkylphosphinic esters were reported on in the previous papers. The present communication reports on the β -methoxyethyl and β -ethoxyethyl esters of α -hydroxyalkylphosphinic acids. The above esters are obtained by the reaction of di- β -methoxyethylphosphoric and di- β -ethoxyethylphosphoric acids with various aldehydes and ketones the reaction, as in the previously reported cases, occurs in the presence of small amounts of alkali metal alcoholates, in particular, sodium methylate. The reaction proceeds rapidly with a great evolution of heat. By analogy to other dialkylphosphoric acids, the mechanism for this reaction can be represented by the following scheme. Sodium alcoholate reacts with di- β -methoxyethylphosphoric acid or di- β -ethoxyethylphosphoric acid to form their sodium salts.



The carbon of the carbonyl group becomes cationic during the reactions because of the shift of electrons, and interacts with the lone pair of electrons on the phosphorus of the sodium salt of the di- β -alkoxyethylphosphoric acid.



and etc., where R is CH_3 and C_2H_5 , and R' and R'', the various radicals of the aldehydes and ketones.

As a result of the reaction, β -methoxyethyl and β -ethoxyethyl esters of α -hydroxyalkylphosphinic acids are formed in accordance with this scheme.

The esters obtained are transparent, syrupy liquids, very often immobile, according to their physical properties.

An attempt to purify the esters obtained by vacuum distillation at 2 mm was unsuccessful. The esters decomposed into the starting materials during distillation. Only the product of the reaction between di- β -methoxyethylphosphoric and di- β -ethoxyethylphosphoric acid and acetone distills with partial decomposition. For this reason it was necessary to choose other methods of purification. The purification of β -methoxymethyl and β -ethoxyethyl- α -hydroxyalkylphosphinic esters was effected by adsorption in simple systems. Fused aluminum oxide and activated charcoal in series served as the adsorbents. Methanol served as the solvent, and in several cases benzene was used. A list of the esters obtained and their constants are given in the Table.

The reaction was also effected with other carbonyl compounds: methylethyl ketone, methylpropyl ketone, acetophenone, benzophenone, benzil, and others. The corresponding β -methoxyethyl and β -ethoxyethyl esters of the α -hydroxyalkylphosphinic acids could not be isolated. Increase in temperature and change in physical properties of the mixture during the experiment indicated that a reaction between these substances had occurred.

TABLE 1

8-Methoxyethyl Esters of α -Hydroxyalkylphosphinic acids

Expt. No.	Starting carbonyl compound	Formula of the substance obtained	n_D^{25}	d_4^{25}	MR _D	
					Found	Calc.
1	Acetaldehyde ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)CH_2CH_3$	1.4401	1.1681	54.61	54.31
2	Butyraldehyde ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)CH_2CH_2CH_2CH_3$	1.4466	1.1365	63.49	63.55
3	Benzaldehyde ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)CH_2C_6H_5$	1.5055	1.2241	73.7	73.8
4	Salicylaldehyde ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)CH_2C_6H_4OH$	1.4975	—	—	—
5	Acetone	$(CH_3OCH_2CH_2O)_2P(=O)(OH)C(CH_3)_2$	1.4365	1.1540	57.97	57.83
5a*	Acetone		1.4345	1.1573	57.67	—
6	Cyclopentanone ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)C(CH_2)_4$	1.4640	1.1910	65.43	65.96
7	Cyclohexanone ..	$(CH_3OCH_2CH_2O)_2P(=O)(OH)C(CH_2)_5$	1.4660	1.1648	70.37	70.5

* The product was isolated by vacuum distillation; b.p. 125-126°(2.5 mm).

TABLE 2

8-Ethoxyethyl Esters of α -Hydroxyalkylphosphinic Acids

Expt. No.	Starting carbonyl compound	Formula of the substance obtained	n_D^{25}	d_4^{25}	MR _D	
					Found	Calc.
1	Acetaldehyde ..	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)CH_2CH_3$	1.4430	1.128	63.5	63.5
2	Butyraldehyde ..	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)CH_2CH_2CH_2CH_3$	1.4476	1.100	72.5	72.7
3	Benzaldehyde...	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)CH_2C_6H_5$	1.4988	1.188	82.0	83.0
4	Salicylaldehyde ..	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)CH_2C_6H_4OH$	—	—	—	—
5	Acetone	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)C(CH_3)_2$	1.4410	1.097	68.3	68.2
6	Cyclopentanone	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)C(CH_2)_4$	1.4570	1.135	75.7	75.2
7	Cyclohexanone	$(C_2H_5OCH_2CH_2O)_2P(=O)(OH)C(CH_2)_5$	1.4562	1.110	79.4	79.8

* B.p. 144-145° (2 mm).

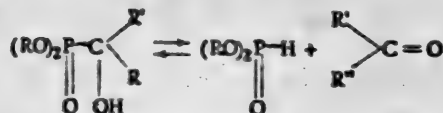
Table 1

Percent phosphorus		Yield (in % of the theoretical)
Found	Calc.	
12.51, 12.78	12.81	79.9
11.67, 11.64	11.48	60.6
10.53, 10.48	10.20	69.7
10.09, 10.00, 9.95	9.69	59.0
12.06, 12.09	12.11	66.4
-	-	-
11.35, 11.42	11.0	66.1
10.51, 10.55	10.47	55.8

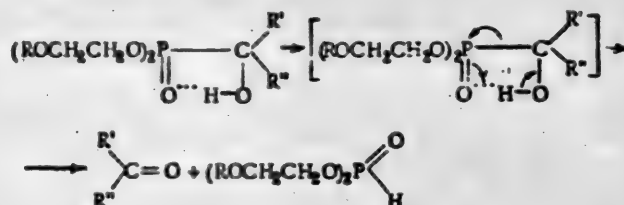
Table 2

Phosphorus content (%)		Yield (in % of the theoretical)
Found	Calculated	
11.7, 11.8	11.5	67.3
10.3, 10.5	10.4	53.1
10.3, 10.3	9.5	69.5
9.0, 9.1	8.9	50.7
10.8, 10.7	10.7	34.0
10.1, 10.2	10.0	53.0
10.5, 10.5	9.5	74.6

During the study of properties of esters of α -hydroxyalkylphosphinic acids it was shown [2], that a decomposition into the starting substances occurs during heating, and that the equilibrium is shifted toward the formation of the starting compounds with increase in temperature.



The ease of rupture of the C-P bond is explained by the presence of a hydroxy group in the α -position and the presence of a hydrogen bond within the ester molecules. With the above studied reaction between di- β -methoxyethylphosphoric and di- β -ethoxyethylphosphoric acids and the above ketones, evidently, an analogous decomposition process of the β -methoxyethyl and β -ethoxyethyl α -hydroxyalkylphosphinic esters which were formed, occurs at the C-P bond. The decomposition of the esters may be represented by the scheme:



where R is CH_3 and C_2H_5 and R' and R'', the various radicals of the ketones.

For this reason it is clear why the corresponding esters of the α -hydroxyalkylphosphinic acids could not be isolated. Their decomposition occurs, apparently, so readily that the heat evolved during the reaction forming them leads to the reverse process. In other cases, evidently, it occurs during the process of purification by the heating. Decrease in the temperature at the time of the purification process in certain cases had a beneficial effect on the preparation of the corresponding esters, for example, during the reaction of di- β -methoxyethylphosphoric acid with cyclohexanone, butyraldehyde, and others. The choice of the temperature during the purification of the α -hydroxyalkylphosphinic esters is of great importance.

EXPERIMENTAL

The experiments were conducted in the following manner. Equimolecular mixtures of di- β -methoxyethylphosphoric, or di- β -ethoxyethylphosphoric acid, and the aldehyde or ketone were prepared, and a small amount of freshly prepared sodium methylate dropped into them. In order to control the course of the reaction, the temperature, refractive index, and the density of the equimolecular mixture of the reacting substances was determined before the addition of the sodium methylate; the sodium methylate was then added and a rise in temperature occurred; at the completion of the reaction

TABLE 3

Course of the Reaction Between Di-*t*-methoxyethylphosphoric Acid and Carbonyl Compounds

Expt. No.	Starting carbonyl compound	Amounts of the reacting substances		Constants of the starting mixture		Increase of temperature during the reaction		n_D^{25} of the mixture after reaction
		Carbonyl compound	Dialkyl-phosphoric acid	n_D^{25}	d_4^{25}	from to		
1	Acetaldehyde.....	2.11	9.5	1.4287	1.085	24	80	1.4390
2	Butyraldehyde.....	3.0	8.0	1.4241	1.044	26	111	1.4400
3	Benzaldehyde.....	4.4	8.0	1.4775	1.133	19	64	1.4952
4	Salicylaldehyde....	2.67	4.2	1.4880	1.167	24	48	1.4848
5	Acetone.....	4.2	12.0	1.4205	1.106	25	80	1.4315
6	Cyclopentanone....	4.0	8.0	1.4337	1.080	16	47	—
7	Cyclohexanone....	4.0	8.0	1.4372	1.079	26	87	1.4285
8	Methylethyl ketone*	3.7	10.0	1.4203	1.074	22	66	1.4235
9	Methylpropyl ketone**	2.17	5.0	1.4190	1.031	21	49	1.4285
10	Acetophenone.....	3.0	5.0	1.4775	1.095	28	57	1.4535
11	Benzophenone.....	3.64	4.0	1.4970	1.139	18	91	1.4960
12	Dibenzyl ketone....	4.36	4.0	1.4970	1.112	23	38	1.4975
13	Benzil 1:1.....	5.3	5.0	—	—	73	120	1.4975
14	Benzil 1:2***.....	9.0	18.8	1.4650	1.1606	24	66	1.4610

* Constants of the reaction product: d_4^{25} 1.1826; n_D^{25} 1.4625; MR_D 62.81; calculated 63.55.** Constants of the reaction product: d_4^{25} 1.091; n_D^{25} 1.4220; MR_D 66.15; calculated 68.17.*** Constants of the reaction product: d_4^{25} 1.1757; n_D^{25} 1.4625; MR_D 66.15; calculated 68.17.

TABLE 4

Course of the Reaction between Di-*t*-ethoxyethylphosphoric Acid and Carbonyl Compounds

Expt. No.	Starting carbonyl compound	Amounts of the reacting substances		Constants of the starting mixture		Increase of temperature during the reaction		n_D^{25} of the mixture after reaction
		Carbonyl compound	Dialkyl-phosphoric acid	n_D^{25}	d_4^{25}	from	to	
1	Acetaldehyde.....	2.4	12.0	1.4229	1.034	23	110	1.4390
2	Butyraldehyde.....	2.8	9.1	1.4230	1.037	21	97	1.4404
3	Benzaldehyde.....	2.1	4.5	1.4696	1.079	21	81	1.4937
4	Sahcylaldehyde.....	2.4	4.7	1.4844	1.119	25	79	1.4441
5	Acetone.....	3.0	9.1	—	—	20	72	—
6	Cyclohexanone.....	2.1	4.5	1.4372	1.045	17	78	1.4562
7	Cyclopentanone.....	2.1	4.5	1.4330	1.043	16	65	1.4512
8	Methylethyl ketone....	1.8	4.5	1.4150	0.997	18	66	1.4225
9	Methylpropyl ketone..	1.3	3.5	1.4191	0.998	20	62	1.4245
10	Acetophenone.....	1.8	4.5	1.4649	1.087	27	109	1.4460
11	Benzophenone.....	3.6	4.5	1.4970	1.102	19	107	1.4956
12	Dibenzyl ketone.....	4.2	4.6	1.4964	1.083	22	40	1.4880
13	Benzil 1:2.....	4.2	9.2	—	—	49	101	1.4828
14	Benzil 1:1.....	4.2	4.6	—	—	63	116	1.4680

the constants were again determined. The purification of the product obtained was then effected.

The purification of the esters was conducted in the following manner. The reaction product was dissolved in 3-4 parts of methyl alcohol, the solution placed into a round bottom flask with a reflux condenser; 10-15 g freshly fused aluminum oxide was then added to the flask. The contents of the flask were heated on the water bath for 1-2

hours. The solution of the product was filtered from the aluminum oxide. Activated carbon was added to the filtrate and it was heated once more for 1-2 hours on the water bath. The carbon was filtered. The filtrate was placed into an Arbuzov flask, the solvent, methyl alcohol, distilled off in vacuum with slight heating. The carbonyl compounds were removed during this operation, if they had not been adsorbed. The constants for the residue were determined. The prepared β -methoxyethyl α -hydroxyalkylphosphinic esters are given in Table 1, and the β -ethoxyethyl hydroxyalkylphosphinic esters in Table 2.

The conditions for the reaction between di- β -methoxyethylphosphoric acid and di- β -ethoxyethylphosphoric acid and compounds containing a carbonyl group are given in Tables 3 and 4.

SUMMARY

1. Di- β -methoxyethylphosphoric and di- β -ethoxyethylphosphoric acid reacted with aldehydes and ketones in the presence of sodium methylate. As a result of the investigation conducted, seven new methoxyethyl and seven new ethoxyethyl esters of various α -hydroxyalkylphosphinic acids were prepared and characterized.

2. Reactions were conducted between di- β -methoxyethylphosphoric and di- β -ethoxyethylphosphoric acids and ketones such as acetophenone, benzophenone, and others. The reaction between them was confirmed by increase in the temperature; however, the corresponding esters of the α -hydroxyalkylphosphinic acids were not obtained, which was explained by the ease of rupture of the C-P bonds in these esters.

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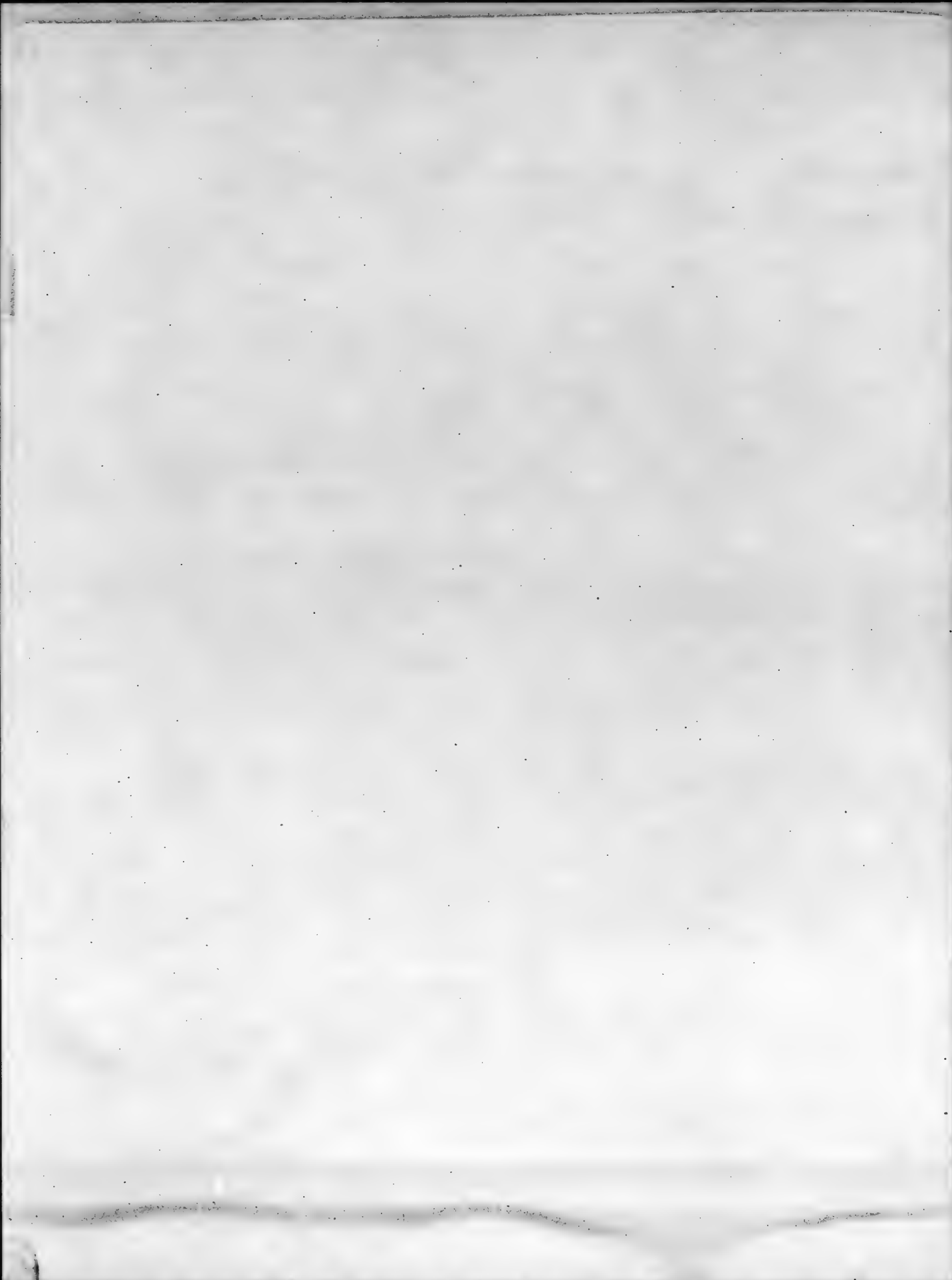
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Received September 6, 1952

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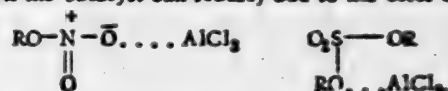
REACTION OF BENZENE WITH ESTERS IN THE PRESENCE OF VARIOUS CATALYSTS

B. V. Tronov and A. M. Petrova

As the many literature results [1,2] and those of the authors' previous investigations [3,4] showed, esters can react with benzene in the presence of catalysts of the type AlCl_3 in two directions: 1) analogous to the alkyl halides, i.e., to form benzene homologs; 2) similar to acid halides, to form ketones in the case of carboxylic esters and nitro compounds in the case of nitrates, etc.

The presence of radicals readily split from oxygen, for example $\text{CH}_3\cdot$ and $\text{C}_2\text{H}_5\text{CH}_2\cdot$, favors the alkylation reaction; with the phenyl radical, stably attached to the oxygen, acylation occurs. As for the acidic residue, then it can be thought that alkylation would occur more readily with esters of strong acids. However, esters of two strong acids, nitric and sulfuric, react differently with benzene. Benzene is nitrated by methyl and ethyl nitrate [5]; with dimethyl sulfate and diethyl sulfate, as was shown by one of the authors [3] and was confirmed by other investigators [6], only alkylation occurs. It is considered possible to explain this difference by the fact that the first stage of the process in both cases is complex formation between the ester and the catalyst with the complex formation occurring differently.

According to the rules of quantum mechanics and the results of physical and chemical investigations, the nitrogen in the so-called compounds with a pentavalent nitrogen is actually a tetravalent positive one. One of the bonds of nitrogen with oxygen in nitro compounds and the alkyl nitrates must be semi-polar. For this reason, the alkyl nitrate combines with the catalyst, primarily, because of the negative charge on the oxygen atom. Sulfur can be fully hexavalent. If the double bond between sulfur and oxygen in the dialkyl sulfate is covalent and not readily capable of forming complexes, then the catalyst can readily add to the ester oxygen as with ethers:



Upon the subsequent reaction with benzene, the nitrate complex is attracted to the carbon of the benzene ring with their nitrogen. This finally leads to the formation of nitrocompounds. The complexes of the sulfate type must react similarly to those of AlCl_3 with hydrocarbon halides or ethers, i.e., in the alkylation direction. Esters of carboxylic acids, evidently, are capable of forming complexes of both types, i.e., the ether of the carbonyl oxygen can participate.

The following problems were posed for the present investigation: 1) to study the reaction of benzene with a large number of different esters and catalysts; 2) to study the course of the reaction using smaller amounts of catalyst than is recommended according to the literature results; 3) to try to separate intermediate complexes between the esters and the catalyst, and benzene with the catalyst and the ester.

The experimental results agree with the above suggestion of two types of complex formation with esters and catalysts. Those esters which were expected to give complex formation resulting from the ether oxygen, gave alkyl benzenes. Esters of boric acid can react in both directions since complexes of the ester with the catalyst can give off alkyls, but boron can also add to the benzene ring. The latter was observed in the experiment with tributyl borate.

The assumed complex compound could not be isolated in experiments with ethyl nitrate. Evidently, for a detailed analysis of the course of the process fine physical methods must be applied, as for example, absorption spectra. However, an indirect proof of the formation of some sort of a complex compound with the ester and SbCl_5 was obtained. The latter itself readily chlorinates benzene. If ethyl nitrate is added initially to benzene, then the subsequent addition of SbCl_5 leads only to nitration. Evidently, SbCl_5 gives a product very rapidly with the nitrate which subsequently reacts with benzene to form nitrobenzene.

EXPERIMENTAL

In most of the experiments, the catalyst was added to 156 g of benzene (2 moles), and then the ester was added. In experiments with SbCl_5 , it was necessary to initially mix the benzene with the ester, and then add the

Expt. No.	Esters	Moles (for 2 moles of C_6H_6)	Catalyst	Moles (for 2 moles of C_6H_6)	Products	Yield in % of the theoretical (based on the ester)
1	C_2H_5ONa	0.5	$AlCl_3$	0.25	$C_6H_5NO_2$	81
2	C_2H_5ONa	0.5	$ZnCl_2$	0.25	$C_6H_5NO_2$	0
3	C_2H_5ONa	0.5	$SnCl_4$	0.25	$C_6H_5NO_2$	29.6
4	C_2H_5ONa	0.5	$SbCl_5$	0.25	$C_6H_5NO_2$	49.2
5	C_6H_5ONa	0.226	$SbCl_5$	0.144	$C_6H_5NO_2$	83.6
6	$SO_2(OC_2H_5)_2$	0.5	$AlCl_3$	0.25	$C_6H_5C_2H_5$ $C_6H_4(C_2H_5)_2$	17 10.9
7	$SO_2(OC_2H_5)_2$	0.5	$FeCl_3$	0.25	The reaction did not occur	
8	$SO_2(OC_2H_5)_2$	0.5	$ZnCl_2$	0.25		
9	$SO_2(OC_2H_5)_2$	0.5	$SnCl_4$	0.25		
10	$SO_2(OC_2H_5)_2$	0.5	$SbCl_5$	0.25		
11	$SO_2(OC_2H_5)_2$	0.5	$BiCl_3$	0.125		
12	$PO(OC_2H_5)_2$	0.25	$AlCl_3$	0.25	$C_6H_5C_2H_5$	23
13	$B(OC_2H_5)_3$	0.5	$AlCl_3$	0.125	Boron organic compound	
14	$Si(OCH_3)_4$	0.17	$SnCl_4$	0.25	The reaction did not occur	
15	$Si(OC_2H_5)_4$	0.125	$AlCl_3$	0.125	$C_6H_5C_2H_5$	12
16	$CH_3COOC_2H_5$	0.125	$AlCl_3$	0.125	The reaction did not occur	
17	$CH_3COOC_2H_5$	0.125	$SbCl_5$	0.125		
18	$CH_3COOC_2H_5$	0.125	$ZnCl_2$	0.125		
19	$CH_3COOC_2H_5$	0.125	$AlCl_3$	0.125		
20	$CH_3COOCH_2C_6H_5$	0.125	$AlCl_3$	0.125	$C_6H_5CH_2C_6H_5$	70.7
21	$CH_3COOCH_2C_6H_5$	0.125	$AlCl_3$	0.125		79.0
22	$CH_3COOCH_2C_6H_5$	0.125	$CuCl_2$	0.125	The reaction did not occur	
23	$CH_3COOCH_2C_6H_5$	0.125	$ZnCl_2$	0.125		
24	$CH_3COOCH_2C_6H_5$	0.125	$ZnBr_2$	0.125		
25	$CH_3COOCH_2C_6H_5$	0.125	$SnCl_4$	0.125		
26	$CH_3COOCH_2C_6H_5$	0.125	$SbCl_5$	0.125	$C_6H_5CH_2C_6H_5$	66.6
27	$CH_3COOCH_2C_6H_5$	0.125	$BiCl_3$	0.125	$C_6H_5CH_2C_6H_5$	36.0
28	$CH_3COOCH_2C_6H_5$	0.125	AlI_3	0.125	$C_6H_5CH_2C_6H_5$	14.0
29	$CH_3COOC_6H_5$	0.125	$AlCl_3$	0.125	The reaction did not occur	11.2
30	$CH_3COOC_6H_5$	0.125	$SbCl_5$	0.125		
31	Triacetin	1/15	$AlCl_3$	0.2	$C_6H_5COCH_3$	28
32	Triacetin	1/15	$SbCl_5$	0.2	$C_6H_5COCH_3$	29
33	$CH_3ClCOOC_2H_5$	0.125	$AlCl_3$	0.125	$C_6H_5C_2H_5$	54.2
34	$CH_3ClCOOCH_3$	0.5	$AlCl_3$	0.125	The reaction did not occur	
35	$(CH_3)_2C=COOC_2H_5$	1/15	$AlCl_3$	1/15	$C_6H_5C_2H_5$	19.2
36	$CH_2=CNCOOCH_3$	0.25	$AlCl_3$	0.125	$C_6H_5C_2H_5$	8.0
37	$CO(OCH_3)_2$	0.125	$AlCl_3$	0.125	The reaction did not occur	
38	$COOC_2H_5COOC_2H_5$	0.125	$AlCl_3$	0.125	$C_6H_5C_2H_5$	15.4
39	$COOC_2H_5CH_2COOC_2H_5$	0.125	$AlCl_3$	0.125	$C_6H_5C_2H_5$	12.5
40	$C_6H_5SO_2OCH_3$	0.125	$AlCl_3$	0.25	$C_6H_5CH_3$	32
41	$C_2H_5OC_2H_5$	0.5	$AlCl_3$	0.125	The reaction did not occur	
42	$C_2H_5OC_2H_5$	0.5	$SbCl_5$	0.125		
43	$C_6H_{11}OC_6H_{11}$	0.125	$AlCl_3$	0.125		
44	$(C_6H_5CH_2)_2O$	0.125	$AlCl_3$	0.125		
45	$(C_6H_5CH_2)_2O$	0.125	$SnCl_4$	0.125	$C_6H_5CH_2C_6H_5$	91.5
46	$(C_6H_5CH_2)_2O$	0.125	$SbCl_5$	0.125	$C_6H_5CH_2C_6H_5$	79.9
					$C_6H_5CH_2C_6H_5$	40.5

catalyst. If the reaction was violent, the mixture had to be cooled at first. Later it was heated for 6 hours on the water bath, water was then added, and sometimes acidified with HCl, and the reaction product was extracted with ether, or steam distilled. The ether-benzene, or benzene solution was dried and distilled through a dephlegmator. The experimental results are given in the Table.

Notes for the Individual Experiments

Nos. 1, 3, 4, 5. Based on the amount of catalyst used, the yield of the product was 162, 59.2, 28.4, and 143%, respectively.

No. 6. The total percent ethylation was $17 + 10.9 \cdot 2 = 38.8\%$.

Nos. 12, 15, 33, 35, 36, 38, 39. Ethyl benzene was converted into acetophenone and its phenylhydrazone.

Nos. 31, 32. A phenylhydrazone with m.p. 104-105° was obtained from the reaction product.

No. 40. The toluene obtained gave 2,4-dinitrotoluene with m.p. 68° upon nitration.

SUMMARY

1. The reaction of benzene with many esters of organic and inorganic acids in the presence of a series of catalysts was studied. Supplementary results on the relation of the direction of the reaction to the nature of the ester and catalyst were obtained.

2. An explanation for the different course of the reaction is given, based on the assumption of different types of complex formation of the ester and the catalyst.

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Received September 19, 1962

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IODINATION OF BENZOIC ACID AND BENZALDEHYDE IN THE PRESENCE OF A NITRIC-SULFURIC NITRATING MIXTURE

B. V. Tronov and A. N. Novitskov

Several methods have been suggested for the preparation of meta-iodobenzoic acid. It is obtained: 1) from benzoic acid by means of the nitro, amino, and diazo compounds; 2) from phthalimide by means of anthranilic and 5-iodoanthranilic acid; 3) by the direct iodination of benzoic acid with iodine in the presence of fuming nitric acid saturated with sulfur trioxide [3] in yields of 55%; from benzoic acid, iodine, concentrated sulfuric acid and silver sulfate [2] in yields of 75%.

The last method gives a good yield of the product but cannot be considered convenient since it requires a great consumption of the valuable reagent (Ag_2SO_4 is used in equimolecular amount with benzoic acid and iodine).

Recently a method of direct iodination in the presence of fuming nitric acid has entered laboratory practice [1] for the preparation of iodobenzene. In the author's laboratory fuming nitric acid was replaced by the usual nitrating mixture prepared from nitric acid of density 1.38-1.40. This method gave the same yield of $\text{C}_6\text{H}_5\text{I}$, with some changes in the conditions of conducting the experiments.

It was decided to apply an analogous method for the iodination of benzoic acid. A large number of experiments were conducted to determine the effect of the ratio of the amounts of benzoic acid, iodine, sulfuric, and nitric acids, the order of addition of the reagents, temperature, and reaction time. It was found that the addition of acetic acid as a solvent had a very beneficial effect, wherein it was found that 80% acetic acid was well as glacial could be used. The strong initial sublimation of iodine was very bothersome and led to a decreased yield and the soiling of the apparatus. A better medium for coping with the sublimation was found to be the addition of carbon tetrachloride. The vapors of the latter were condensed in the colder parts of the apparatus and the flowing CCl_4 returned the iodine to the reaction mixture. An inexpensive and simple method for the isolation and purification of the product was also developed. As a result, constant yields of 75% meta-iodobenzoic acid were achieved in the best experiments. The melting point and the results of the determination of the halogen, according to Stepanov, proved the purity of the acid. A qualitative test for nitrogen gave a negative result.

The same reaction was studied with benzaldehyde because of interest in the oxidizing action of nitric acid. The iodination of the aldehyde under the same conditions as were used with benzoic acid led only to the preparation of meta-iodobenzoic acid, but with a lower yield. Therefore, in addition to the iodination of the benzene ring, the oxidation of the aldehyde group to the carboxyl occurred. Since the greatest oxidative properties are possessed not by nitric acid, but by the nitrous acid and nitrous oxide formed from it, the iodination of benzaldehyde was conducted with the addition of urea. Meta-iodobenzaldehyde was obtained in yield up to 20%, which cannot be considered the maximum since the effect of various conditions on this process has not been sufficiently determined.

EXPERIMENTAL

Iodination of benzoic acid. The benzoic acid, iodine, solvents, and in certain experiments, sulfuric acid were mixed in a 200 ml three-necked flask with fittings for a condenser, dropping funnel, and stirrer with a seal. The mixture was heated to the desired temperature on a sulfuric acid bath (with thermoregulator). The nitric acid or a mixture with sulfuric acid was then added gradually with stirring. The heating was continued after the addition of the HNO_3 . Crystals of iodobenzoic acid gradually formed in the homogenous liquid, nitrous oxide was evolved, and the liquid became lighter. The iodine subliming during the experiment was washed down with the carbon tetrachloride into the reaction mixture. The mixture was stirred from time to time.

At the end of the experiment, the mixture was transferred into a beaker, and the precipitate was washed into it with distilled water. More water was added to the beaker, and some more crystals precipitated. The crystals were then separated by filtration and washed, first with cold water, and then with hot. A mixture, evidently, of unreacted benzoic acid and iodobenzoic acid precipitated in the filtration flask. After washing, the product was recrystallized from aqueous alcohol (50%) 2 or 3 times. Meta-iodobenzoic acid with m.p. 185-187° was obtained.

Found (according to Stepanov) %: I 50.6, 50.8. $\text{C}_7\text{H}_5\text{O}_2\text{I}$. Calculated %: I 51.17.

The results of the experiments are given in the Table.

Effect of Conditions on the Yield of Meta-Iodobenzoic Acid

C ₆ H ₅ COOH	Amount in moles			Amount (in ml)		Temperature	Time (in hours)	Yield (in % of the theoretical)
	I ₂	HNO ₃	H ₂ SO ₄	CH ₃ COOH	CCl ₄			
0.15	0.075	0.6	0.6	50	—	125°	4	35.1
0.15	0.075	0.3	0.3	50	—	125	4	48.0
0.15	0.075	0.15	0.15	50	—	125	4	50.0
0.15	0.075	0.9	0.9	50	—	125	4	0
0.05	0.025	0.075	0.075	15	4	85	7	58.2
0.05	0.025	0.0625	0.0675	15	4	85	7	66.3
0.05	0.025	0.05	0.1	15	4	85	7	74.0
0.05	0.025	0.0375	0.1125	15	4	85	7	69.2
0.05	0.025	0.025	0.125	15	4	85	7	63.6
0.05	0.025	0.025	0.1	15	4	85	5	43.3
0.05	0.025	0.0375	0.1	15	4	85	5	51.3
0.05	0.025	0.05	0.1	15	4	85	5	66.0
0.05	0.025	0.1	0.1	15	4	85	5	67.5
0.05	0.025	0.15	0.1	15	4	85	5	68.2
0.05	0.025	0.05	0.05	15	4	85	5	14.0
0.05	0.025	0.05	0.075	15	4	85	5	42.5
0.05	0.025	0.05	0.1	15	4	85	5	65.0
0.05	0.025	0.05	0.125	15	4	85	5	60.1
0.05	0.025	0.05	0.15	15	4	85	5	55.8
0.05	0.025	0.075	0.075	15	4	75	4	38.5
0.05	0.025	0.075	0.075	15	4	85	4	56.2
0.05	0.025	0.075	0.075	15	4	100	4	46.0
0.05	0.025	0.075	0.075	15	4	125	4	24.5
0.05	0.025	0.05	0.1	15	4	85	2	36.1
0.05	0.025	0.05	0.1	15	4	85	3	58.5
0.05	0.025	0.05	0.1	15	4	85	4	63.0
0.05	0.025	0.05	0.1	15	4	85	5	65.0
0.05	0.025	0.05	0.1	15	4	85	6	69.4
0.05	0.025	0.05	0.1	15	4	85	7	74.0
0.05	0.025	0.05	0.1	15	4	85	8	71.6
0.5	0.25	0.562	1	150	40	85	7	75.3

Iodination of benzaldehyde. 10.1 ml of C₆H₅CHO, 12.69 g of iodine, 20.67 ml of HNO₃, and 16.71 H₂SO₄ were used. Temperature, 85°, experiment time 6 hours. Without acetic acid and urea, only benzoic acid was isolated; with 30 ml of glacial CH₃COOH, 51.3% of meta-iodobenzoic acid were obtained. 4.6 g (20%) of meta-iodobenzaldehyde with m.p. 58° was obtained in an experiment with 30 ml of CH₃COOH and 8 g urea. The phenylhydrazone obtained from the aldehyde had an m.p. 156°.

SUMMARY

1. A method for the synthesis of meta-iodobenzoic acid by the action of iodine on benzoic acid in the presence of a nitric-sulfuric nitrating mixture was developed. A stable yield of not less than 75% of the theoretical was obtained. The given method is simpler and less expensive than the methods for the preparation of meta-iodobenzoic acid reported in the literature.

2. The suggested method is also applicable for the preparation of meta-iodobenzaldehyde. It is only necessary to add urea, without which the oxidation of the aldehyde group to the carboxyl occurs.

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Received September 19, 1952

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CATALYTIC ALKYLATION OF ANILINE WITH ETHYL ALCOHOL

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The preparation of alkyl and dialkylanilines in the presence of aluminum oxide, thorium oxide, promoted aluminum oxide, and other oxide catalysts has been studied by a series of investigators [1]. The properties of natural aluminum silicate, bentonite was studied by one of the authors. It was shown that this clay, the main part of which is montmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{nH}_2\text{O}$, was a catalyst for the dehydration of alcohols [2] and for the simultaneous dehydration of alcohols and acid anhydrides [3]. Because of this fact it seemed of interest to determine whether it was possible to apply bentonite as a catalyst for the simultaneous dehydration of alcohols and aniline in order to obtain alkylanilines. It was shown that, at 350°, a molar ratio of aniline to ethyl alcohol of 1:2, and a volume velocity of 0.15, a yield of ethyl aniline up to 87-89% of the aniline reacted was obtained.

In addition, for the preparation of esters, activated carbon, soaked with phosphoric acid, conditionally called "solid phosphoric acid" later [4] was used. It was shown that in the presence of this catalyst, good yields of propyl and butyl acetates and butyrates are obtained by the mutual dehydration of alcohols and acids in the vapor phase. This made it possible to suppose that "solid phosphoric acid" could be used as dehydration catalyst for the reaction of aniline with alcohol.

In the present investigation it was shown that the alkylation of aniline with alcohol could be accomplished in the presence of "solid phosphoric acid" with the predominant formation of ethylaniline. The yield of ethylaniline at 275° volume velocity 0.3, and a molar ratio of aniline to alcohol of 1:2 to 1:5 was 59-62% of the aniline reacted.

EXPERIMENTAL

Experiments on the alkylation of aniline were conducted in a general apparatus for effecting reactions in the vapor phase by the flow method. The reaction mixture was prepared from freshly distilled, initially well dried aniline and ethyl alcohol. At the end of the experiment (for a better separation of the catalyzate) a stream of nitrogen was passed for 30-40 minutes. The catalyzate obtained consisted of two layers: an aqueous alcohol layer and an amine layer. The latter was thoroughly dried over fused potassium hydroxide and distilled. The fraction boiling up to 160° was discarded (unreacted alcohol and traces of aniline). The fraction, 160-235°, was subjected to further investigation, and consisted of unreacted aniline, ethylaniline, and diethylaniline.

The freshly distilled reaction product was analyzed by a method developed for the determination of primary amines in mixtures of amines [5].

The temperature, the ratio of components, and the rate of passage of the reaction mixture were varied in order to find the optimum conditions for the formation of ethylaniline over bentonite and "solid phosphoric acid".

Alkylation of Aniline in the Presence of Bentonite.

Commercial bentonite activated with sulfuric acid and preheated in a catalytic furnace to 400-430° was used for the reaction.

The effect of the temperature and the ratio of the reaction components on the yield of ethylaniline.

A mixture of aniline and ethyl alcohol in molar ratios of 1:1, 1:1.5, 1:2, and 1:2.5 was used. The reaction mixture was passed over the catalyst at a constant velocity of 0.15 at temperatures of 350-450°. At temperatures below 350° the alkylation reaction of aniline proceeded with small yields.

From the data given in Table 1, it follows that the largest yield of ethyl aniline occurs at 350° and ratios of aniline to alcohol of 1:1.5, 1:2. A further increase of the temperature and the concentration of the alcohol causes a gradual decrease in the yield of the alkylaniline. The catalyzate obtained distilled almost completely at 180-212°, and only a small amount distilled at a higher temperature (to 235°). This indicated that the alkylation product of aniline was ethylaniline, with a very small impurity of diethylaniline.

TABLE 1

Experiment temperature (in °C)	Percent of aniline transformed at ratios of aniline to alcohol of			
	1:1	1:1.5	1:2	1:2.5
350	80.7	86.5	87.2	81.2
375	77.5	79.5	80.4	77.9
400	73.2	73.7	74.3	74.0
425	67.8	71.0	72.2	69.9
450	64.1	66.3	70.5	67.5

TABLE 2

Experiment temperature (in °C)	Volume velocity	Percent aniline transformed
350	0.07	83.6
350	0.15	87.2
350	0.30	27.0

TABLE 3

Experiment temperature	200°	250°	275°	300°	350°	400°
Percent of aniline transformed at a ratio of reacting substances of 1:1	23.6	37.7	49.5	37.7	30.0	16.0
Percent of aniline transformed at a ratio of reacting substances of 1:1.5	38.6	53.6	58.6	52.0	26.7	21.0

TABLE 4

Composition of the catalyzate (in %)

Experiment temperature	250°	275°	300°
Aniline	46.4	41.4	48.0
Ethylaniline	47.8	54.4	48.7
Diethylaniline	5.8	4.2	3.3

Effect of the rate of the passage of the reaction mixture on the yield of ethylaniline. The following experiments were conducted as the above, at the passage of the mixture of aniline-alcohol with a volume velocity of 0.15. In order to determine the effect of the velocity of passage of the mixture on the yield of ethylaniline, the volume velocity was decreased to 0.07, and then increased to 0.30.

The results of the experiments are given in Table 2, from which it follows that the increase of the volume velocity from 0.07 to 0.15 has little effect on the yield of the ethylaniline upon alkylation of aniline over bentonite. Further increase of the velocity of passage of the reaction mixture to 0.30 causes a sharp decrease in the yield of ethylaniline.

Alkylation of Aniline in the Presence of "Solid Phosphoric Acid"

The catalyst used for this investigation was prepared by a method which was reported for the preparation of esters [4].

Effect of temperature on the yield of ethylaniline. Two series of experiments were set up: the first with a molar ratio of aniline to alcohol of 1:1, and the second with a ratio, 1:1.5.

The experiments were conducted at temperatures of 200-400° and volume velocity of passing the reaction mixture of 0.1. The results of these experiments are given in Table 3.

Diethylaniline, as well as aniline, was determined in the catalyzates obtained from experiments conducted at 250, 275, and 300° (Table 4).

On the basis of these experiments it can be concluded that:

1) the optimum temperature for the ethylation of aniline under these experimental conditions is 275° (Table 3); the decrease in the yield of ethylaniline with the further increase of the temperature was explained by the strong decomposition of the alcohol which was proved by special experiments;

2) ethylation reaction of aniline over the given catalyst proceeds mainly in the direction of the formation of ethylaniline; diethylaniline was obtained in small quantities, and its yield decreased with decreasing temperatures (Table 4).

TABLE 5

Volume velocity of the passage of the reaction mixture	0.1	0.3	0.6	1.0
Percent of aniline transformed	58.6	65.15	54.6	53.2

TABLE 6

Molar ratio of aniline:alcohol	1:1	1:1.5	1:2	1:4	1:5	1:6
Yield of crude catalyate(in%)	82.5	80.0	80.0	75.0	68.9	60.7
Amount ethylaniline in the catalyate(in %)	55.2	65.2	73.5	82.0	90.2	94.8
Yield ethylaniline on the aniline reacted (in %)	45.5	52.0	59.0	61.5	62.0	57.5

Effect of the velocity of passage of the reaction mixture on the yield of ethylaniline. The experiments were conducted at the optimum temperature of 275° and at a ratio of the components of 1:1.5; the volume velocity of the passage of the reaction mixture was varied from 0.1 to 1.0.

From the results given in Table 5, it follows that increasing the velocity of passage of the reaction mixture does not sharply affect the yield of ethylaniline; however, the best yield occurs at the passage of the mixture of aniline-alcohol with a volume velocity of 0.3.

Effect of the quantitative ratio of the reacting components on the yield of ethylaniline. In order to determine this effect, a series of experiments was set up with various mixtures in which the molar ratio of the aniline and the alcohol was varied from 1:1 to 1:6. All of the experiments in this series were conducted at 275° and a volume velocity of the passage of the mixture of 0.3. The results are given in Table 6.

From the results given in Table 6 it follows that the yield of ethylaniline in the catalyate is 94-95% when there was a large excess of alcohol to the aniline (1:6), but a considerable part of the alcohol was decomposed to ethylene, which did not react; the yield of the catalyate was only 60% under these conditions. For this reason the most satisfactory mixture of aniline and alcohol to use was a ratio of 1:2, with which the yield of the aniline in the catalyate was somewhat lower, 73.5% but, based on the aniline reacted was almost always constant at 57.5-59%.

On the basis of the experiments conducted it can be considered completely established that "solid phosphoric acid" can be used satisfactorily for the alkylation reaction of aniline with ethyl alcohol.

SUMMARY

1. The catalysts employed in this investigation, bentonite and "solid phosphoric acid", caused mutual dehydration in the system aniline-alcohol. Ethylaniline is mainly formed as a result of this dehydration; diethylaniline is only formed in small amounts.
2. The optimum conditions for the preparation of ethylaniline over bentonite are 350°, a ratio of aniline to alcohol of 1:2, and a volume velocity of passing the reaction mixture of 0.15. Under these conditions, the yield of ethylaniline is 87% of the aniline reacted.
3. The optimum conditions for the preparation of ethylaniline over "solid phosphoric acid" are: 275°, ratio of aniline to alcohol of 1:2, and a volume velocity of passage of the reaction mixture of 0.3. Under these conditions, the yield of ethylaniline was 59% of the aniline reacted.

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Received January 24, 1953

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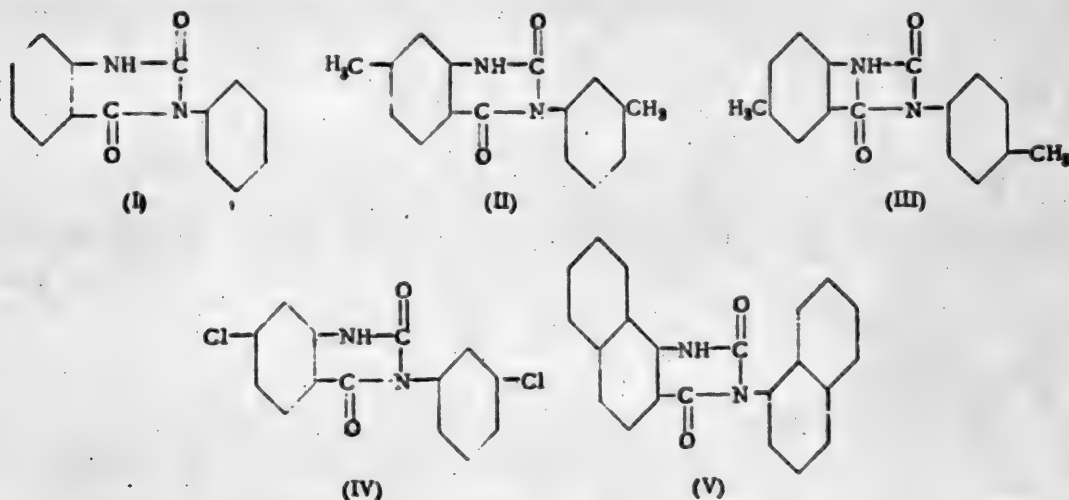
INTRODUCTION OF A CARBOXYL GROUP INTO AROMATIC AMINES

A. I. Kizber and A. S. Glagoleva

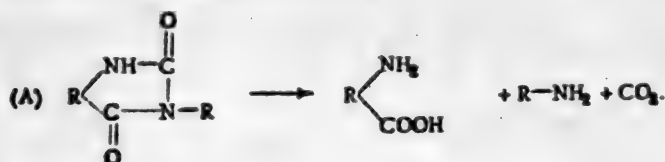
One of the authors showed that, by heating aromatic amines with carbon dioxide and alkali metal carbonates, or certain chlorides, the formation of very small amounts of amino carboxylic acids occurred. Thus if aniline was heated at 170-180° under CO₂ pressure in the presence of K₂CO₃, Na₂CO₃, or CaCl₂, o- and p-aminobenzoic acids could be isolated.

Upon further investigation, it was found that the amino carboxylic acids were obtained with relatively better results if N-acyl derivatives were used instead of the free aromatic amines [1,2]. The latter were heated with K₂CO₃ under CO₂ pressure to 185-260°. The maximum yield achieved was 25% of theory based on the amine used, and about 80% based on the amine recovered. o- and p-aminobenzoic acids were obtained from acetanilide, diphenylurea (symm.), benzanilide, and phenyl isocyanate; from acet-p-toluidine, 3-methyl-6-aminobenzoic acid; from 3,3'-dimethyldiphenylurea, 4-methyl-6-aminobenzoic acid; from 3,3'-dichlorodiphenylurea, 4-chloro-6-aminobenzoic acid; from acet-1-naphthylamine, 1,2- and 1,4-naphthylamine carboxylic acid.

o-Aminocarboxylic acids were obtained at the end of the reaction to a great extent in the form of derivatives of 2,4-dioxotetrahydroquinazoline.



The latter are cleaved into the corresponding o-aminocarboxylic acids and amines by heating for several hours with 5-10% solutions of alkalis.

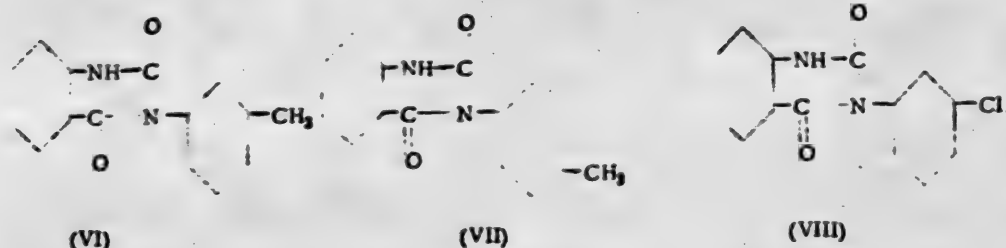


The formation of derivatives of 2,4-dioxotetrahydroquinazoline during the process of heating N-acylamines with K₂CO₃ under CO₂ pressure only became comprehensible when it was found that these compounds can be obtained by heating salts of o-aminocarboxylic acids under CO₂ pressure. Thus (I) was obtained from potassium anthranilate, and (III), from potassium p-toluidine-o-carboxylate.

Since a partial decarboxylation always occurs during the heating of salts of o-aminocarboxylic acids, and amines are formed, the conversion of o-aminocarboxylic acids into derivatives of 2,4-dioxotetrahydroquinazoline can be represented by a scheme which is the reverse of scheme (A).

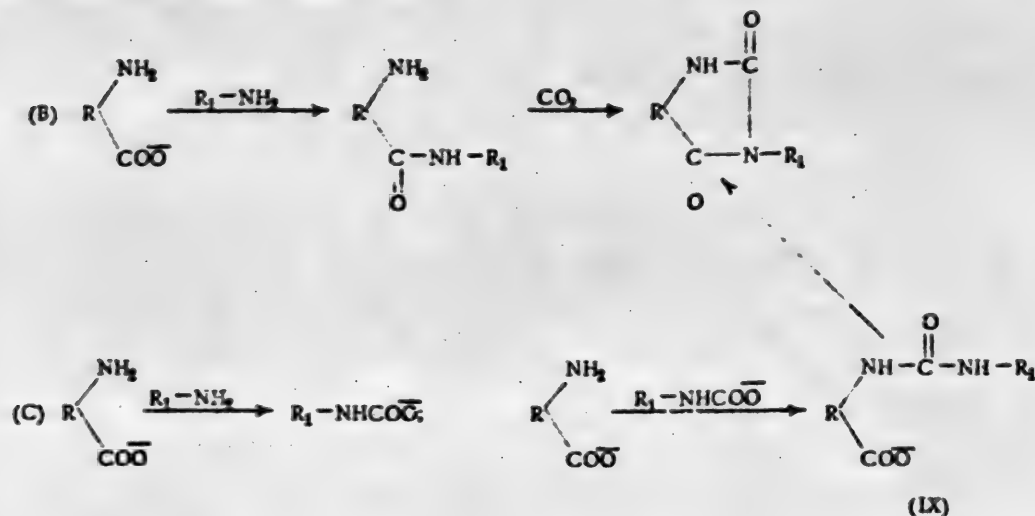
If this scheme is correct, the formation of various 2,4-dioxotetrahydroquinazolines could be expected upon heating salts of o-aminocarboxylic acid with various amines.

Actually, heating, for example, potassium anthranilate under CO_2 pressure with m-toluidine, p-toluidine, and m-chloroaniline resulted in the following, respectively:



Several compounds of this type are reported in the literature, they are obtained by the condensation of o-aminocarboxylic acids with amines which contain a carbonyl group on the nitrogen. Derivatives of urea and the corresponding isocyanates [3] are equivalent to such amines.

The preparation of derivatives of 2,4-dioxotetrahydroquinazoline from salts of o-aminocarboxylic acids under CO_2 pressure appeared possible by the aid of one of the following schemes:



A test of scheme (B) gave negative results. The formation of quinazoline derivatives did not occur when the amide of anthranilic acid was heated under CO_2 pressure.

The isolation of product (IX) would have been a direct proof for scheme (C). Attempts to isolate (IX) however, as it could be expected, were unsuccessful. It is known that anthranilides of aryl amino-N-carbamic acids are transformed at $100\text{--}120^\circ$ into derivatives of 3-phenyl-2,4-dioxotetrahydroquinazoline, whereas the synthesis reported was conducted at above 200° ; under these conditions the presence of a noticeable amount of (IX) can scarcely be expected.

An indirect proof of the correctness of scheme (C) is the formation of salts of aryl-N-carbamic acids during the process of the above reported transformation. Thus, after heating potassium anthranilate in a sealed tube to $220\text{--}230^\circ$, potassium phenyl-N-carbamate was found. p-Toluidine, when treated in a sealed tube with calcium anthranilate, gives rise to 4,4'-dimethylphenylurea. The obtaining of the latter is difficult to explain without assuming that the formation of p-tolyl-N-carbamic acid occurred initially.

Salts of aryl-N-carbamic acid were also found during the process of preparing aminocarboxylic acids by heating N-acylarylamines under carbon dioxide pressure. If the given process is conducted at temperatures somewhat lower than necessary for the formation of aminocarboxylic acids, then the yield of salts of aryl-N-carbamic acids attains a value of 80% of theory in a series of cases. It must be mentioned that potassium salts of aryl-N-carbamic acids are obtained by heating N-acylarylamines with K_2CO_3 under conditions of normal pressure.

Potassium salts of acyl N-carbamic acids form aminocarboxylic acids above 180° when the corresponding CO_2 pressure is used, when proceeding in open vessels at temperatures above 200°, they decompose with the evolution of CO_2 , amine, and evidently, the di-potassium salt of aryl-N-carbamic acids.

It is completely apparent that, in the synthesis of aminocarboxylic acids from N-acylarylamines, salts of aryl-N-carbamic acids are not side products, but intermediates, whose interaction with CO_2 results in the aminocarboxylic acids.

EXPERIMENTAL

Experiments under pressure were conducted in a steel 400 ml autoclave equipped with an anchor stirrer, a socket for a thermometer, a monometer, needle valve for releasing pressure, and tube for the introduction of CO_2 .

Example of the Preparation of 3-Phenyl-2,4-dioxotetrahydroquinazoline (I) and Aminobenzoic Acids.
106 g of symm-diphenylurea and 140 g of K_2CO_3 were heated under CO_2 pressure (50-65 atm) for 5 hours at 250-255°. The reaction products were mixed with 350 ml of water, and the insoluble part filtered. 10.5-11 g of p-aminobenzoic acid with traces of anthranilic acid were obtained by acidifying the filtrate to pH 6-6.5. By recrystallization from water, 7.7-7.8 g of p-aminobenzoic acid with m.p. 184-185° was obtained. The water-insoluble product, which was impure (I), was heated for 3 hours with 10% KOH, filtered, and acidified to pH 5.5-6; 6.5-7 g of anthranilic acid with m.p. 144-145° was obtained. A mixed sample with pure anthranilic acid melted at 144-145°. 6-7 g of the copper anthranilate was precipitated from filtrates with copper sulfate, which was treated with 20 ml of 2-3% sodium hydroxide, filtered, and an additional amount of anthranilic acid with m.p. 144.5-145° was isolated.

In order to obtain pure (I), the impure product was treated with dilute hydrochloric acid, filtered, and the residue washed with water until neutral. 10.5 g of a substance with m.p. 273-274° was obtained; platelets with m.p. 276-277° (275-277° [4]) from glacial acetic acid.

3.84% mg substance: 9.970 mg CO_2 ; 1.424 mg H_2O . 3.132 mg substance: 8.149 mg CO_2 ; 1.206 mg H_2O .
3.666 mg substance: 0.390 ml N_2 (729 mm, 23.8°). 2.764 mg substance: 0.290 ml N_2 (739 mm, 18.0°).
Found %: C 70.82, 71.00; H 4.15, 4.31; N 11.72, 11.96. $C_{14}H_{10}O_2N_2$. Calculated %: C 70.69; H 4.20; N 11.76.

The product is soluble in strong alkali with blue fluorescence, and upon heating of its alkaline solutions splits into anthranilic acid and aniline.

3-(3'-Methylphenyl)-2,4-dioxo-7-methyltetrahydroquinazoline. (II) and 2-Amino-4-methylbenzoic acid.
150 g of 3,3'-dimethyldiphenylurea and 100 g of K_2CO_3 were heated for 6 hours under CO_2 pressure (38-40 atm) at 220-230°. The reaction products were mixed with 250 ml of water, left to settle, and the oily layer separated. The latter was shaken for 10 minutes with 200 ml of 4% KOH (35-40°), left to settle, and the brown aqueous layer separated. 20 g of (II) precipitated on acidification. Platelets with m.p. 294-295° from glacial acetic acid.
6.204 mg substance: 16.416 mg CO_2 . 3.080 mg H_2O . 5.942 mg substance: 15.728 mg CO_2 ; 2.824 mg H_2O . 3.990 mg substance: 0.380 ml N_2 (729 mm, 23.8°). 2.919 mg substance: 0.255 ml N_2 (727 mm, 20°). Found %: C 72.20, 72.23; H 5.55, 5.38; N 10.51, 10.34. $C_{17}H_{14}O_2N_2$. Calculated %: C 72.14; H 5.26; N 10.52.

1.5 g of the product was heated for 3 hours with 70 ml of 10% KOH. On cooling, it was filtered from a small precipitate. The filtrate was extracted several times with ether. The aqueous residue of the extraction was adjusted to pH 6-6.5 with hydrochloric acid. About 0.45 g of 2-amino-4-methylbenzoic acid with m.p. 175-177° deposited; platelets with m.p. 176-177° (157° [5]) from aqueous alcohol. A mixed sample with pure 2-amino-4-methylbenzoic acid melted at 176-177°.

3-(4'-Methylphenyl)-2,4-dioxo-6-methyltetrahydroquinazoline (III) and 6-amino-3-methylbenzoic acid.

100 g of acet-p-toluidine and 100 g of K_2CO_3 were heated for 8 hours at 255-260° under CO_2 pressure. The reaction products were boiled for 3 hours with 300 ml of 5% KOH. They were filtered and 11-11.5 g of 6-amino-3-methylbenzoic acid was precipitated by acidification; platelets with m.p. 172-173° (172.5 [6]) from 50% alcohol.

3.004 mg substance: 6.970 mg CO_2 ; 1.608 mg H_2O . 3.904 mg substance: 9.084 mg CO_2 ; 2.170 mg H_2O .
4.945 mg substance: 0.419 ml N_2 (728 mm, 21°). 3.319 mg substance: 0.280 ml N_2 (727 mm, 22°).
Found %: C 63.32, 63.64; H 5.99, 6.22; N 9.42, 9.33. $C_{14}H_{13}O_2N$. Calculated %: C 63.6; H 5.96; N 9.3.

By diazotization and boiling of the hydrochloric acid solution, 6-hydroxy-3-methylbenzoic acid with m.p. 149-150° (149-150° [7]) was obtained.

If the reaction mixture was acidified with hydrochloric acid after autoclaving, to a strong acid reaction to Congo, about 5 g of 3-(4'-methylphenyl)-2,4-dioxo-6-methyltetrahydroquinazoline (III) was obtained; crystals with m.p. 285-286° from 80% acetic acid.

3.312 mg substance: 8.767 mg CO_2 ; 1.492 mg H_2O . 3.702 mg substance: 9.784 mg CO_2 ; 1.736 mg H_2O .
5.862 mg substance: 0.528 ml N_2 (744 mm, 24°). 3.357 mg substance: 0.310 ml N_2 (744 mm, 23°).
Found %: C 72.19, 72.05; H 5.04, 5.25; N 10.14, 10.42. M 283. $C_{16}H_{15}O_2N$. Calculated %: C 72.14; H 5.26; N 10.52; M 266.

The product was soluble in alkali with a blue fluorescence; it was cleaved to 6-amino-3-methylbenzoic acid, p-toluidine, and small amounts of the alkali-insoluble p-toluidide of 6-amino-3-methylbenzoic acid by a 2-hour boiling with 10% KOH. The last product was recrystallized from dilute acetic acid and melted at 182°; it gave an orange color upon the addition of a hydrochloric acid solution of nitrite to it; upon boiling in hydrochloric acid, it was cleaved to p-toluidine and 6-amino-3-methylbenzoic acid.

4.738 mg substance: 0.483 ml N_2 (746.3 mm, 21.4°). 2.685 mg substance: 0.290 ml N_2 (741 mm, 23°).
Found %: N 11.87, 11.82. $C_8H_9ON_2$. Calculated %: N 11.66.

3-(3'-Chlorophenyl)-2,4-dioxo-7-chlorotetrahydroquinazoline (IV).

140 g of 2,6'-dichlorodiphenylurea and 90 g of K_2CO_3 were heated for 14 hours under CO_2 pressure (49-50 atm) to 240-245°. The oily reaction product was shaken with 400 ml of water, and the lower oily layer was separated from the water in a separatory funnel. 3 g of (IV) was isolated by treatment with dilute hydrochloric acid; platelets with m.p. 311-312° from a mixture of acetic acid and alcohol. Pure 3-(3'-chlorophenyl)-2,4-dioxo-7-chlorotetrahydroquinazoline melted at 312°. A mixed sample melted at 311-312°. The product was soluble in dilute alkali with a blue fluorescence.

(IV) was heated for 2 hours with a 10% NaOH solution, filtered, and the alkaline filtrate was extracted with ether. The aqueous residue from the extraction was acidified with hydrochloric acid to a pH of 6.5-7, and extracted with ether. Upon removal of the ether a residue of 4-chloroanthranilic acid was obtained; platelets with m.p. 234-235° (235-236° [8]) from 50% alcohol. A mixed sample with pure 4-chloroanthranilic acid melted at 234-235°.

3-(1-Naphthyl)-2,4-dioxo-7,8-benzotetrahydroquinazoline (V). Naphthylamine carboxylic acid. 92.5 g of acet-1-naphthylamine and 138 g of K_2CO_3 were heated under CO_2 pressure (20-25 atm) for 6 hours at 185-195°. The reaction mass was mixed with 350 ml of water and filtered. About 1.4 g of 1,4-naphthylaminocarboxylic acid was isolated by the neutralization of the filtrate; crystals with m.p. 177° (177° [9]) from dilute alcohol.

3.160 mg substance: 8.176 mg CO_2 ; 1.347 mg H_2O . 2.944 mg substance: 7.609 mg CO_2 ; 1.304 mg H_2O .
3.727 mg substance: 0.254 ml N_2 (741 mm, 25.5°). 3.681 mg substance: 0.242 ml N_2 (742.7 mm, 24°).
Found %: C 70.57, 70.49; H 4.70, 4.96; N 7.59, 7.39. $C_{11}H_9O_2N$. Calculated %: C 70.59; H 4.81; N 7.48.

1,4-Hydroxynaphthoic acid with m.p. 179° (183-184° [10]) was obtained by diazotizing and boiling of the hydrochloric acid solution.

The water-insoluble product was boiled for 10 hours with 400 ml of 5% NaOH, filtered, and acidified. About 8 g of naphthylamine-2-carboxylic acid precipitated; platelets with m.p. 203-205° (205° [11]) from 30% alcohol.

3.440 mg substance: 8.858 mg CO_2 ; 1.490 mg H_2O . 3.120 mg substance: 8.017 mg CO_2 ; 1.342 mg H_2O .
3.673 mg substance: 0.251 ml N_2 (728 mm, 23.6°). 4.282 mg substance: 0.291 ml N_2 (735 mm, 21.4°).
Found %: C 70.27, 70.12; H 4.85, 4.81; N 7.54, 7.65. $C_{11}H_9O_2N$. Calculated %: C 70.59; H 4.81; N 7.48.

1-Hydroxy-2-naphthoic acid with m.p. 184-185° (185-186° [12]) was obtained by diazotization and boiling

of the hydrochloric acid solution.

A dye was obtained by coupling of the diazo compound with 2-naphthol, which in contrast to dyes prepared from diazo-1,4-naphthylamine carboxylic acid, was insoluble in dilute alkalis.

To isolate (V), the reaction mixture, after autoclaving, was mixed with 5% NaOH, and filtered; the product precipitates after acidification of the filtrate. It was mixed with 100 ml of concentrated ammonia, filtered, and washed with water to neutrality. About 5 g of (V) was obtained; needles with m.p. 333-334° from glacial acetic acid.

3.302 mg substance: 9.453 mg CO₂; 1.250 mg H₂O. 3.716 mg substance: 10.643 mg CO₂; 1.432 mg H₂O.

3.750 mg substance: 0.273 ml N₂ (733.3 mm, 22°). 3.034 mg substance: 0.225 ml N₂ (732.6 mm, 22.6°).

Found %: C 78.12, 78.16; H 4.24, 4.31; N 8.12, 8.26. C₂₂H₁₄O₂N₂. Calculated %: C 78.11; H 4.14; N 8.28.

The product was soluble in dilute alkalis; it was cleaved to 1-naphthylamine and naphthylamine-2-carboxylic acid by boiling with alkali.

Experiments on the mutual heating of potassium anthranilate and various arylamines. 120 g of potassium anthranilate and 170 g of m-chloroaniline was heated for 6 hours at 220-220° under CO₂ pressure (30 atm). The reaction mass was acidified to Congo with dilute hydrochloric acid. 6 g of 3-(3'-chlorophenyl)-2,4-dioxotetrahydroquinazoline (VIII) was obtained; narrow interwoven platelets with m.p. 260.5-261.5° from 50% acetic acid. The product contained a small amount of 3-phenyl-2,4-dioxotetrahydroquinazoline (I), from which it could not be separated by many recrystallizations.

5.590 mg substance: 12.802 mg CO₂; 1.862 mg H₂O. 5.806 mg substance: 13.299 mg CO₂; 1.926 mg H₂O.

4.159 mg substance: 0.397 ml N₂ (734 mm, 28°). 3.641 mg substance: 0.346 ml N₂ (737.35 mm, 28°).

Found %: C 62.48, 62.46; H 3.73, 3.76; N 10.44, 10.47; Cl 11.98. C₁₄H₉O₂N₂Cl. Calculated %: C 61.65; H 3.36; N 10.27; Cl 13.03.

The structure of the product was proved by its cleavage to anthranilic acid and m-chloroaniline by boiling with sodium hydroxide solution.

0.4 g of the substance was heated for 2 hours with 10 ml of 10% NaOH. The m-chloroaniline formed was extracted with ether; anthranilic acid with m.p. 144-145° was precipitated in the aqueous residue by adjustment to pH 6-6.5. A mixed sample with anthranilic acid melted at 145°.

m-Chloroaniline was identified by converting it to an azo dye, for which the ether extract was treated with dilute hydrochloric acid, diazotized, and the diazo compound coupled with 2-naphthol. A dye was obtained (scale-like platelets from glacial acetic acid) with m.p. 155-156°. The crystals from pure m-chloroaniline and 2-naphthol melted at 155-157°. A mixed sample melted at 155-157°.

100 g of potassium anthranilate and 150 g of m-toluidine were heated for 5 hours at 225-230° under CO₂ pressure (26-28 atm.). The reaction mixture was acidified to Congo with dilute hydrochloric acid. The precipitate which separated was mixed with 200 ml of 5% NaOH and filtered. About 7.5 g of the product with m.p. 225-230° was isolated from the filtrate by acidifying to Congo. Two recrystallizations from 50% acetic acid with activated carbon resulted in spindle-like crystals of 3-(3'-methylphenyl)-2,4-dioxotetrahydroquinazoline (VI) with m.p. 252-252.6°.

5.356 mg substance: 14.018 mg CO₂; 2.276 mg H₂O. 5.562 mg substance: 14.510 mg CO₂; 2.304 mg H₂O.

0.1950 g substance: 15.64 ml 0.1N HCl. 0.2154 g substance: 17.17 ml 0.1N HCl. Found % C 71.40;

71.42; H 4.75, 4.64; N 11.23, 11.16. C₁₅H₁₃O₂N₂. Calculated %: C 71.43; H 4.76; N 11.11.

0.6 g of the substance was boiled for 4 hours with 15 ml of 10% KOH, diluted with water, and about 0.1 g of a silvery precipitate, the m-toluidide of anthranilic acid, m.p. 113-114° (113-114° [13]) was filtered. A mixed sample with pure anthranilic acid m-toluidide melted at 113-114°. m-Toluidine was extracted with ether from the filtrate, and anthranilic acid with m.p. 144-145° was isolated upon adjustment to pH 6-6.5. A mixed sample with pure anthranilic acid melted at 144-145°.

100 g of potassium anthranilate and 150 g of p-toluidine were heated for 7 hours at 230-235° under CO₂ pressure (27-30 atm). A precipitate formed by acidifying the reaction products with dilute hydrochloric acid, which was treated with 5% NaOH solution. A small precipitate was filtered; thin needles of 4,4'-dimethyldiphenylurea with m.p. 262° (262-263° [14]) were obtained by recrystallization first from acetic acid, and then from alcohol. A mixed sample with pure 4,4'-dimethyldiphenylurea melted at 262.5°.

12.2 g of a substance with m.p. 240-245° was isolated from the alkaline filtrate by acidifying to Congo; needles of 3-(4'-methylphenyl)-2,4-dioxotetrahydroquinazoline (VII) were obtained from glacial acetic acid, which melted at 249-250° initially, then solidified, and once more melted at 259-260° (259-260° [5]).

* The insoluble product was filtered out and washed with water to neutrality.

6.080 mg substance: 15.882 mg CO₂; 2.610 mg H₂O. 6.548 mg substance: 17.107 mg CO₂; 2.922 mg H₂O.
3.250 mg substance: 0.303 ml N₂ (733.2 mm, 19°). 4.276 mg substance: 0.407 ml N₂ (732.4 mm, 20°). Found %:
C 71.28, 71.30; H 4.80, 4.99; N 10.51, 10.69. C₁₅H₁₂O₂N₂. Calculated %: C 71.43; H 4.76; N 11.11.

1 g of the product was refluxed in a flask for 6 hours with 25 ml of 10% KOH. As the heating progressed, the solution clouded and p-toluidine droplets (m.p. 44°) formed in the condenser. At the end of this time, it was filtered. There was about 0.15 g of anthranilic acid p-toluidide, m.p. 149-150° (151° [16]) in the residue. Anthranilic acid, m.p. 144-145°, was liberated by acidification of the alkaline filtrate. A mixed sample with pure anthranilic acid melted at 144-145°.

15 g of potassium anthranilate was heated for 8 hours at 230-240° in a 175 ml sealed glass tube. A pressure was detected upon opening the tube at the end of the experiment. The reaction products were treated with hydrochloric acid. 1 g of 3-phenyl-2,4-dioxotetrahydroquinazoline (I) melting at 276-277° was obtained. A mixed melting point with (I) obtained by heating diphenylurea with K₂CO₃ under CO₂ pressure gave no depression.

10 g of potassium 2-amino-4-methylbenzoate was heated for 8 hours in a sealed tube at 220-230°. Pressure was observed upon opening the tube. The reaction products were processed in the previous manner. About 0.6 g of 3-(4'-methylphenyl)-2,4-dioxotetrahydroquinazoline (II) was obtained. Crystals with m.p. 285-286° from acetic acid. A mixed sample with (III) obtained by heating acet-p-toluidide with K₂CO₃ under CO₂ pressure melted at 285-286°.

Potassium aryl-N-carbamates. 106 g of diphenylurea and 138 g of K₂CO₃ were heated in the autoclave for 8 hours at 175-180° under CO₂ pressure (30-40 atm). A white powder was obtained, which was the potassium salt of phenyl-N-carbamic acid with impurities of K₂CO₃ and a small amount of unreacted diphenylurea. The yield of potassium N-phenylcarbamate was about 80% of theory. The product was treated with pyridine, filtered, and washed with ether to remove the impurity of diphenylurea.

15 g of the substance purified in this manner was heated to 40° with 45 ml of pyridine, 20 ml of methyl benzenesulfonate was added over a 3 hour period, the reaction mass was kept for 1 hour at 50°, cooled, filtered, the filtrate evaporated in vacuum (15 mm) on the boiling water bath, acidified to Congo with hydrochloric acid, and extracted with ether. Methyl phenyl-N-carbamate remained after the removal of the ether; needles with m.p. 47° (47° [17]) from 50% alcohol. A mixed sample with pure methyl phenyl-N-carbamate melted at 47°.

3.394 mg substance: 7.970 mg CO₂; 1.870 mg H₂O. 3.680 mg substance: 8.643 mg CO₂; 1.950 mg H₂O.
3.650 mg substance: 0.283 ml N₂ (749.2 mm, 21°). 3.922 mg substance: 0.299 ml N₂ (748.8 mm, 21°).
Found %: C 64.08, 64.10; H 6.17, 5.93; N 8.88, 8.72. C₈H₉O₂N₂. Calculated %: C 63.57; H 5.96; N 9.27.

15 g of 3,3'-dichlorodiphenylurea, 11 g of K₂CO₃, and 30 ml of m-chloroaniline were heated for 10 hours at 185-190° with efficient stirring in a flask equipped with a straight condenser in a slow stream of CO₂. The residue was freed from the residual 3,3'-dichlorodiphenylurea by treatment with pyridine, filtration, and washing with ether. Potassium-3-chlorophenyl-N-carbamate contaminated with K₂CO₃ was obtained. Yield about 50% of theoretical. The product was soluble in alkalis. Upon standing in alkaline solution, hydrolysis occurred with formation of 3-chloroaniline.

SUMMARY

1. On heating N-acylarylamines with K₂CO₃ under CO₂ pressure, aminocarboxylic acids, derivatives of 3-phenyl-2,4-dioxotetrahydroquinazoline, and salts of aryl-N-carbamic acids were formed; the latter were also obtained upon heating a series of N-acylarylamines in the absence of CO₂ under normal pressure.
2. 3-Phenyl-2,4-dioxotetrahydroquinazoline and its derivatives were formed by heating potassium salts of aromatic o-aminocarboxylic acid; on heating potassium anthranilate with a series of arylamines, derivatives of 3-phenyl-2,4-dioxotetrahydroquinazoline were formed.
3. In view of the fact that, during the process of heating N-acylarylamines with K₂CO₃ under CO₂ pressure, some of them are transformed to an 80-85% extent, to the potassium salt of aryl-N-carbamic acid before the start of the formation of aminocarboxylic acids, as well as the fact that heating potassium salts of phenyl-N-carbamic acids leads to the formation of aminocarboxylic acids, it is quite apparent that salts of aryl-N-carbamic acids are not side, but intermediate, reaction products, which are the source of the formation of ions of arylamines which react with CO₂ and form amino acids.

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Received January 24, 1963.



INVESTIGATION OF CONJUGATED SYSTEMS

XLVII. CONDENSATION OF BUTYNONE WITH CYCLIC DIENIC HYDROCARBONS

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Of the large number of papers on "dienic syntheses", an insignificant number is about investigations on the condensation of dienic compounds with acetylenic aldehydes, ketones, acids, and derivatives of acids [1]. Only several condensations of dienic compounds with acetylene dicarboxylic and phenylpropionic acids and their derivatives have been reported, as well as those in which propionic, tetrollic, and phenylpropionic aldehydes participated [2-4]. The authors of this communication studied the reactions of the simplest acetylenic ketone, butynone, with divinyl, isoprene, piperylene, dipropenyl, diisopropenyl, and chloroprene [5-7]. Several dienic syntheses with the participation of butynone, and other acetylenic ketones (propylacetylenyl ketone, phenylacetylenyl ketone, propenylacetylenylketone, dibenzoylacetylene) were reported by foreign chemists [8, 9]. Recently an unusual condensation of butynone with methylcyclohexanones by another scheme was reported.

Continuing the investigation of the reactions of butynone with dienic compounds, experiments were conducted on the condensation of this substance with cyclic dienic hydrocarbons, cyclopentadiene-1,3 and cyclohexadiene-1,3.

Previously the condensation of these hydrocarbons with acetylenic compounds was studied only with vinylacetylenyl ketone, acetylene dicarboxylic acid, its esters, and nitrile [11-17].

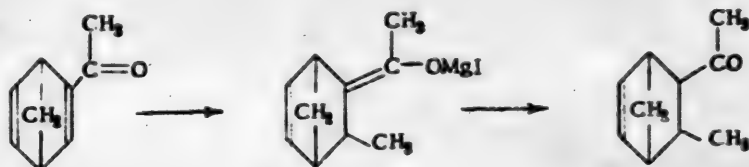
Cyclopentadiene, with all of these compounds, gives even at room temperature, comparatively stable condensation products with endo-methylene bridges, which decompose into the starting components upon heating [11-14].

Cyclohexadiene at 0° gives a normal condensation product with acetylene dicarboxylic acid, a dibasic acid with an endo-ethylene bridge. However, this product readily loses an ethylene molecule on heating and gives phthalic acid [15]. The condensation of cyclohexadiene with acetylene dicarboxylic acid esters at 200° gives phthalic acid esters directly [16].

The experiments conducted showed that cyclopentadiene readily condenses with butynone even at 50° with the formation of two products as a result of the reaction, a liquid and a crystalline substance.

The liquid product was found to be the normal condensation product of cyclopentadiene and butynone, 1-acetyl-3,6-endomethylene-cyclohexadiene-1,4 which readily formed a semicarbazone.

Attempts to obtain tertiary alcohols from this ketone by the action of methyl magnesium iodide and bromide under conditions previously used for the synthesis of tertiary alcohols from cyclohexadienic ketones [17] ended unsuccessfully. A ketone with another methyl group was obtained instead of the alcohol. Evidently, the organo magnesium compound added to the starting ketone at the conjugated system of bonds according to the scheme:

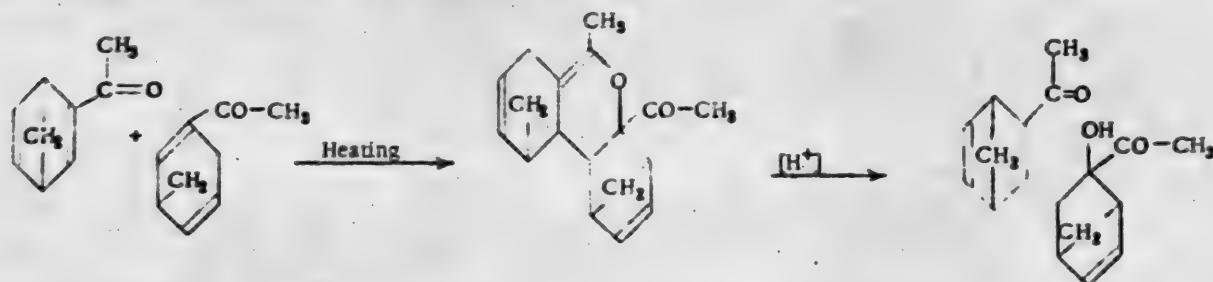


Such an addition of organo magnesium compounds occurs very frequently during reactions with α,β -unsaturated ketones [18].

The ketone obtained, 1-methyl-2-acetyl-3,6-endomethylenecyclohexene-4, readily formed a well crystallizing semicarbazone and 2,4-dinitrophenylhydrazone.

The crystalline condensation product with m.p. 107° was found to be the dimer of the liquid ketone. It was readily obtained from the latter by heating, as well as by prolonged storage. Each redistillation of the liquid ketone (at 10mm) was accompanied by the formation of small amounts of this crystalline dimer in the distillation flask. The dimer distills at 183-185° without apparent decomposition at 10 mm. The substance has the same empirical formula as the liquid ketone but a double molecular weight, it gives a positive result upon testing for the presence of a carbonyl group (reaction with p-nitrophenylhydrazine), and does not contain hydroxyl groups (determined according to Terentyev).

Acetylendomethylenecyclohexadiene can form a dimer analogous to that of methylacrolein [19] resembling the reaction of acrolein with vinyl ethers [20], namely according to the scheme:

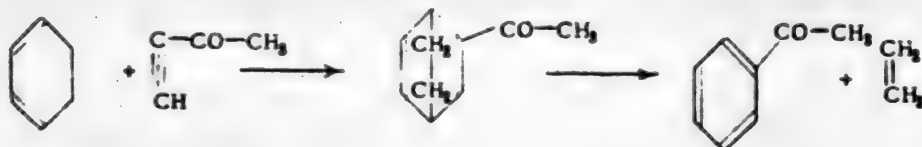


The proposed formula for the dimer was proved by its relation to acids. It readily rearranged by the action of acids to a substance with a higher melting point containing two carbonyl groups (it gives a double p-nitrophenylhydrazine) and a hydroxyl group (determined according to Terentyev, giving a result two times the theoretical amount evidently because the organo magnesium compound causes the dehydration of the substance).

The formation of the dimer from the condensation products of cyclopentadiene with α,β -unsaturated carbonyl compound had not been found up to the present investigation.

Cyclohexadiene practically does not condense with butynone at 50°. At 90°, the reaction proceeds slowly, forming acetophenone and ethylene as the main products. In addition to acetophenone, a very small amount of a higher boiling substance was formed, which, however, was not isolated in pure state. Apparently, this is the normal product of the condensation with an endo-ethylene bridge. At 120°, the reaction proceeds with the formation of acetophenone and ethylene exclusively. Acetophenone was identified by constants and melting point of its 2,4-dinitrophenylhydrazone. Ethylene was absorbed by bromine and identified as dibromoethane.

Therefore, the condensation of butynone and cyclohexadiene is accompanied by the cleavage of the endo-ethylene bridge by the scheme:



EXPERIMENTAL

Butynone was obtained for the investigation by shaking methoxy or ethoxyvinylacetylene with 5g H_2SO_4 (for 8-10 g of the ether, 100-120 ml of the acid was used) until complete solution [21]. The solution obtained was saturated with ammonium sulfate, and the butynone extracted with several portions of toluene. The subsequent experiments were conducted with these solutions dried with anhydrous sodium sulfate.

Cyclopentadiene was obtained by the slow distillation of the dimer; cyclohexadiene, by the distillation of 1,2-dibromocyclohexane with quinoline. Cyclohexadiene contained cyclohexene as an impurity which did not interfere in the subsequent experiments since cyclohexene does not condense with butynone under the usual conditions of the dienic synthesis.

1. Condensation of cyclopentadiene with butynone.

In one of these experiments 13.5 g (17 ml) of cyclopentadiene was heated in a sealed glass tube for 6 hours at 90° with a solution of butynone in toluene prepared from 16 g of ethoxyvinylacetylene. By vacuum distillation (toluene was removed at 50 mm and the residue was distilled at 10 mm), 12 g of a liquid product (90-95°) and 5 g of residue were obtained which boiled at 183-185° and crystallized upon standing.

The liquid reaction product came over mainly at 92° (20 mm) upon redistillation and had

d_4^{20} 1.0362, n_D^{20} 1.5098. MR_D found: 38.71. $C_9H_{10}O$. Calculated: 38.44.

0.1312 g substance: 0.3862 g CO_2 ; 0.0894 g H_2O . Found %: C 80.33; H 7.62. $C_9H_{10}O$. Calculated %: C 80.56; H 7.51.

The substance polymerized partly upon redistillation, and upon standing, with the formation of a crystalline product (identical with that isolated directly from the reaction mixture) and tars. A semicarbazone with m.p. 166-167° was obtained from the substance. It could not be recrystallized. A ketone (4.3 g) with b.p. 94.5-95° at 20 mm was obtained in 55% yield by the reaction of 7 g of the substance with two equivalents of an ether solution of methyl magnesium iodide under the usual conditions.

d_4^{20} 0.9905, n_D^{20} 1.4846. Found MR_D 43.44. $C_{10}H_{14}O$. Calculated 43.52.

8.59 mg substance: 25.33 mg CO_2 ; 7.23 mg H_2O . Found %: C 80.47; H 9.47. $C_{10}H_{14}O$. Calculated %: C 79.86; H 9.40.

A semicarbazone and 2,4-dinitrophenylhydrazone were obtained from the ketone under the usual conditions. The semicarbazone was recrystallized from aqueous alcohol. M.p. 170°.

9.78 mg substance: 1.616 ml N_2 (16°, 770 mm). Found %: N 19.78. $C_{11}H_{14}ON_2$. Calculated %: N 19.27.

The 2,4-dinitrophenylhydrazone had an m.p. 182.5-183.5° (it was recrystallized from dilute a.c.).

3 g of the ketone was distilled with a 10% solution of oxalic acid; the substance distilled unchanged. Therefore, it was shown that it did not contain any tertiary alcohol as an impurity.

The same ketone with b.p. 92-94° at 20 mm was obtained by the action of a double quantity of an ether solution of methyl magnesium bromide upon acetylenedimethylenecyclohexadiene; d_4^{20} 0.9886, n_D^{20} 1.4886.

The crystalline product of the condensation of cyclopentadiene with butynone was washed with several portions of cold methanol, it then weighed 3.5 g. After recrystallization from methyl alcohol the substance melted at 107° and was a white dense crystalline substance.

0.1292 g substance: 0.3788 g CO_2 ; 0.0880 g H_2O . 0.1308 g substance: 0.3860 g CO_2 ; 0.0882 g H_2O .
0.1206 g substance: 20.0 g benzene: Δt 0.115°. Found %: C 80.01, 80.53; H 7.62, 7.54; M 268.5.
 $C_{12}H_{16}O_2$. Calculated %: C 80.56; H 7.51; M 268.3.

The substance gave a binary p-nitrophenylhydrazone with m.p. 182-183° with p-nitrophenylhydrazine in acetic acid, which corresponded in analytical data to the p-nitrophenylhydrazone of the product of hydrolysis of the starting substance.

6.88 mg substance: 0.871 ml N_2 (17°, 762.5 mm). 8.90 mg substance: 1.185 ml N_2 (18°, 749 mm).
Found %: N 14.95, 15.39. $C_{13}H_{18}O_2N_2$. Calculated %: N 15.10.

Upon heating 1 g of the substance with 5 ml of acetic acid for 30 minutes and after neutralization of the mixture with sodium carbonate, about 0.9 g of product was obtained which melted at 127-128° after recrystallization from aqueous acetone.

7.20 mg substance: 19.90 mg CO_2 ; 5.18 mg H_2O . 9.24 mg substance: 25.48 mg CO_2 ; 6.45 mg H_2O .
0.1386 g substance: 16.57 g benzene: Δt 0.152°. Found %: C 75.43, 75.25; H 8.05, 7.81; M 284.4.
 $C_{14}H_{20}O_2$. Calculated %: C 75.49; H 7.74; M 286.3.

* Without recrystallization.

The determination of the active hydrogen according to Terentyev gave twice the calculated result.
0.0376 g substance: 6.94 ml CH_4 (15°, 751 mm). 0.0440 g substance: 7.80 ml CH_4 (18°, 755 mm).
Found number of active H atoms: 2.04. 2.06. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{OH}$. Calculated 1.0.

The same binary p-nitrophenylhydrazone, m.p. 182-183° (without recrystallization) was obtained from the substance with m.p. 127-128° in acetic acid as was obtained from the substance with m.p. 107°, however, with a poorer yield.

6.63 g substance: 0.863 ml N_2 (18°, 750.5 mm). Found %: N 15.08. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$. Calculated %: N 15.10.

Upon heating cyclopentadiene (8 g) with butynone (from 7.6 g of ethoxyvinylacetylene) at 50° for 6 hours, 6.2 g of a liquid and about 1 g of a crystalline product was obtained.

2. Condensation of cyclohexadiene with butynone.

a) 12 g of cyclohexadiene was heated for 6 hours in a sealed tube with a toluene solution of butynone obtained from 12 g of ethoxyvinylacetylene. After distillation at reduced pressure of the toluene and the reagents, no higher boiling residue remained in the flask.

b) The same amounts of the reagents were heated for 10 hours at 100-105°. After the removal of the toluene, 4 g of a substance remained in the flask, which was separated into the following fractions upon distillation (10 mm): 1) 80-85°, 2 g; 2) 85-91°, 1 g; 3) 91-93°, 0.8 g. The last fraction had n_D^{25} 1.5212.

The first fraction was found to be acetophenone. The last fraction had constants which differed from those found for acetophenone (b.p. 83-85° at 12 mm, d_4^{25} 1.0236, n_D^{25} 1.5342) [22]. However this fraction gave a 2,4-dinitrophenylhydrazone, which was characteristic for acetophenone dinitrophenylhydrazone with m.p. 236°. Evidently, the substance is a mixture of acetophenone and the normal product of the condensation.

c) Upon heating the same quantities of the reagents at 120° for 6 hours, 6 g of acetophenone was obtained (yield 40%) with b.p. 94.5° at 20 mm, d_4^{25} 1.0290, n_D^{25} 1.5344; the p-nitrophenylhydrazone of the substance melted at 184°, the 2,4-dinitrophenylhydrazone at 237°, which accurately corresponded to the literature data. A pressure was detected when the tube was opened. Several of the tubes were cooled with a mixture of ice and salt prior to opening, and the gas which was evolved after their opening, was passed into bromine. A small amount of dibromoethane with b.p. 131-133° and n_D^{25} 1.5380 was obtained. Literature data: [22], b.p. 131.7°, n_D^{25} 1.5379.

SUMMARY

1. The condensation of butynone with cyclopentadiene-1,3 and cyclohexadiene-1,3 was studied.
2. It was shown that cyclopentadiene gave a normal condensation product, 1-acetyl-3,6-endomethylene-cyclohexadiene-1,4, capable of being transformed into a crystalline dimer, constructed analogously to that of methylacrolein, upon heating and upon storage.
3. It was shown that cyclohexadiene condensed with butynone with the cleavage of a molecule of ethylene to form acetophenone.

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Received December 25, 1952

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* See Consultants Bureau Translation, p. 949.



INVESTIGATIONS OF CONJUGATED SYSTEMS

XLVIII. ORDER OF ADDITION OF ALKYL HYPOIODITES TO CHLOROPRENE HOMOLOGS

A. A. Petrov and E. A. Leporskaya

Investigation of reactions of chloroprene and bromoprene with alkyl hypohalites conducted by one of the authors led to unexpected results. It was found that the order of addition depends on the nature of the halogen. Alkyl hypochlorites added to chloroprene and bromoprene mainly at the ends of the conjugated system [1,2], i.e., in a similar manner as halogens [3,4,5] and hydrogen halides [6,7,8] add to these substances, with the chlorine entering position one. Alkyl hypobromites and hypoiodites added almost exclusively to the unsubstituted double bond with the halogen atoms entering position 4 [9,10,11]. Therefore, only alkyl hypochlorites were found able to polarize the entire dienic system as a whole.

This eccentricity in the reactions of chloroprene and bromoprene with alkyl hypohalites was explained by steric and energetic factors. Chlorine or bromine atoms in position 2 of the chloroprene and bromoprene molecules, possibly, interfere with the entrance of bromine and iodine atoms into position 1, whereas this barrier is insufficient for the entrance of chlorine. It is possible that here the great heat of reaction of alkyl hypochlorites with dienes is of effect because of which a more complete polarization of the systems exists in the reaction complex.

The necessity to establish the mechanism of this effect caused the authors to investigate the order of addition of alkyl hypohalites to homologs of chloroprene and bromoprene. The present communication deals with the investigation of the order of addition of alkyl hypoiodites to homologs of chloroprene with radicals in the α -position of the conjugated system $R-CH=CCl-CH=CH_2$.

α -Alkyl derivatives of chloroprenes were first prepared by the addition of hydrogen chlorides to α -alkyl derivatives of vinylacetylene [12]. The latter was prepared by the action of alkylating agents on sodium derivatives of vinyl acetylene in liquid ammonia [13]. This method was used.

The chemical properties of the chloroprene homologs were scarcely studied. Authors who first obtained these compounds only investigated their condensation with naphthoquinone and polymerizations. Up to now, no one had studied these compounds.

5 substances were prepared for the investigation, whose formulas and constants are given in Table 1. Two substances were previously unsynthesized.

TABLE 1

Substance	B.p. (°C)	Pressure (mm)	d_4^{20}	n_D^{20}	MRD		Literature
					Found	Calculated	
$CH_2=CH-CCl=CH-CH_3$	100	760	0.9592	1.4782	30.72	29.22	[13]
	99.5-101.5	759	0.9576	1.4785	30.33	29.22	
$CH_2=CH-CCl=CH-C_2H_5$	122.5-123.5	760	0.9392	1.4772	35.09	33.84	[13]
	68.2-69	117	0.9390	1.4770	35.08	33.84	
$CH_2=CH-CCl=CH-C_3H_7$	49.5-50.5	20	0.9290	1.4798	39.93	38.46	-
$CH_2=CH-CCl=CH-C_4H_9$	69.5-70.5	20	0.9185	1.4782	44.58	43.08	[13]
	64-65	18	0.9366	1.4794	43.82	43.08	
$CH_2=CH-CCl=CH-(CH_2)_7-$ $-CH(CH_3)_2$	83.5-84.5	20	0.9134	1.4770	49.08	47.70	-

and tertiarybutylvinylacetylene could not be obtained; in both cases, hydrogen halide was cleaved from the halogen derivative to form propylene and isobutylene, respectively.

In addition to isobutylene, a hydrocarbon derived from isobutyl bromide was obtained in very low yields.

TABLE 6

Substance	Weight of sample (g)	Weight AgCl (g)	%Cl	
			Found	Calculated
$\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	0.1301	0.1424	27.08	27.15
	0.1246	0.1360	27.42	27.15
$\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}(\text{CH}_2)_2-\text{CH}(\text{CH}_3)_2$	0.1340	0.1193	22.02	22.34

Further experiments were not conducted with these substances. Propylene and butylene were identified as dibromides: the gas which separated, after the absorption of ammonia with water and dilute acid, was passed into a bromine solution.

Dibromopropane had the following constants: b. p. 141-142°; d_4^{20} 1.3344; n_D^{20} 1.5202. Literature data: b. p. 141.6°; d_4^{20} 1.9333.

Dibromomethylpropane had the following constants: b. p. 150-151°; d_4^{20} 1.7676; n_D^{20} 1.5100. Literature data [15]: b. p. 149-151°; d_4^{20} 1.7627; n_D^{20} 1.5119.

II. Preparation of Chloroprene Homologs

1 Mole of the hydrocarbon, 220 ml of hydrochloric acid, saturated with hydrogen chloride, at 0°, 0.25 mole of CuCl_2 , and 0.2 moles of methylamine hydrochloride, or ammonium chloride (0.2 g of hydroquinone) were shaken for 9 hours, the water layer was separated, the oil washed with water, dried over CaCl_2 , and fractionated through a dephlegmator.

The yields of the chloroprenes boiling within 1-2° were: 3-chloropentadiene-1,3 (36%) 3-chlorohexadiene-1,3 (27%) 3-chloroheptadiene (36%), 2-chlorooctadiene and 3-chloro-7-methyloctadiene-1,3 (15%), based on the hydrocarbon used. The unreacted hydrocarbons were once more hydrochlorinated. The total yield for two consecutive hydrochlorinations was 27% for chlorooctadiene and chloromethyloctadiene. Table 6 gives the analytical results for the new compounds prepared.

III. Iodoalkoxylation of Chloroprene Homologs

1. Iodomethoxylation of 3-chloropentadiene-1,3. 48 g of mercuric oxide was added to a solution of 29.5 g chloropentadiene (0.2 g hydroquinone) in 80 ml of methyl alcohol, and 74 g of powdered iodine was added slowly with efficient stirring and cooling (temperature of the reaction mixture, 10-12°) in 5 g portions. After the addition of each portion of iodine, the mixture was shaken and stirred until decolorization. At the end of the reaction, the unreacted mercuric oxide and the mercuric iodide were filtered and washed with alcohol on the filter, the filtrate was diluted with water, the oil which separated was washed with calcium chloride solution to remove the alcohol, dried over CaCl_2 and vacuum distilled. The fractions were obtained (5 mm): 1) 70-80°-6 g, 2) 82-83°-39 g and 3) residue, 3.5 g. Yield of the main fraction, 52% of theory. The constants of the substance are in Table 2, the analytical data in Table 7.

2. Iodomethoxylation of 3-chlorohexadiene-1,3. An oil was obtained under the above conditions from 24 g of chlorohexadiene, 60 ml of methyl alcohol, 33.5 g of mercuric oxide, and 52.6 g of iodine, which gave the following fractions upon distillation (at 10 mm): 1) 80-90°-1.9 g, 2) 90-100°-1.6 g, 3) 100-104°-3.5 g, 4) 104-106°-17 g, 5) 106-110°, 3.1 g, 6) residue, 4.2 g. Yield of the main (100-110°) fraction, 42.7% of theory. Constants are given in Table 2, analytical data in Table 7.

About 4 g of propionic and 4 g of oxalic acids were obtained after the usual processing of the mixture, by the oxidation of 33 g of the iodoether at 10° with 760 ml of a 5% potassium permanganate solution, to which 8 g more of permanganate was added in small portions. The propionic acid was converted into an anilide with m.p. 104°; in addition a p-toluidide with m.p. 123° was also obtained from it. Neither crystalline product gave any depression in mixed melting point with authentic preparations of propionic acid anilide and p-toluidide.

3. Iodoethoxylation of chlorohexadiene. 13 g of a substance was obtained from 10 g of chlorohexadiene, 60 ml of ethyl alcohol, 14 g of mercuric oxide, and 22 g of iodine, which gave the following fractions upon distillation (10 mm): 1) up to 107°-1.0 g, 2) 107-109°-10.4 g, 3) 109-111°-1.5 g.

Constants of the main part of the substances are given in Table 2, analytical data, in Table 7.

4. Iodomethoxylation of chloroheptadiene. An oil was obtained from 20 g of chloroheptadiene, 60 ml of alcohol, 35 g of mercuric oxide, and 57 g of iodine, which gave the following fractions upon distillation (10 mm): 1) to 114°-6 g; 2) 114-117°-40 g; 3) residue, 4 g. Yield of the main fraction, 63%. The constants are given in Table 2, analytical results in Table 8.

TABLE 4

Substance	B.p. (°C)	Pres- sure (mm)	d_4^{20}	n_D^{20}	MR _D		Melting point		
					Found	Calcu- lated	Semi- carba- zone	p-nitro- phenyl- hydra- zone	2,4-di- nitro- phenyl- hydra- zone
$\text{CH}_3\text{COCCl}=\text{CH}_2$	38-40	30	1.1373 (15°)	1.4608 (15°)	25.21	25.08	139- 140	100-103	—
$\text{CH}_3\text{COCCl}=\text{CHCH}_3$	65-66	30	1.0966	1.4742	30.33	29.70	—	122	188
$\text{CP}_3\text{COCCl}=\text{CHC}_2\text{H}_5$	76-77.5	30	1.0592	1.4730	35.12	34.32	—	—	139
$\text{CH}_3\text{COCCl}=\text{CHC}_3\text{H}_7$	91-93	30	1.0301	1.4720	39.85	38.94	—	111.5- 112	144
$\text{CH}_3\text{COCCl}=\text{CHC}_4\text{H}_9$	108-111	30	1.0070	1.4705	44.55	43.56	—	117-118	108
$\text{CH}_3\text{COCCl}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	118-120	30	0.9836	1.4662	49.21	48.18	168	105	131
$\text{CH}_3\text{COCClB}=\text{CH}_2\text{Br}$	83-83.5	10	2.0084	1.5375	41.15	41.15	—	—	—
$\text{CH}_3\text{COCClB}=\text{CHBrCH}_3$	94.5-95	10	1.8689	1.5348	46.36	45.70	—	—	—

TABLE 5

Substance	B.p. (°C)	Pressure	d_4^{20}	n_D^{20}	MR _D	
					Found	Calculated
$\text{CH}_2=\text{CHC}\equiv\text{C}-\text{CH}_3$	59-59.5	760	0.7396	1.4450	23.72	22.77
	59.2	760	0.7401	1.4496 ²³	23.98	22.77
	80.5-84	760	0.7479	1.4522	28.91	27.34
$\text{CH}_2=\text{CHC}\equiv\text{C}-\text{C}_2\text{H}_5$	84.5-85.3	—	0.7492	1.4522 ²³	28.86	27.34
	109.5-110	760	0.7603	1.4524	33.43	32.00
$\text{CH}_2=\text{CHC}\equiv\text{C}-\text{C}_3\text{H}_7$	44.3-44.7	75	0.7671	1.4520 ¹⁴	33.00	32.00
	62-64	60	0.7763	1.4568	37.93	36.61
$\text{CH}_2=\text{CHC}\equiv\text{C}-\text{C}_4\text{H}_9$	62-63	61	0.7830	1.4592 ²³	37.84	36.61
$\text{CH}_2=\text{CHC}\equiv\text{C}-\text{CH}_2\text{CH}(\text{CH}_3)_2$	54-56	60	0.7668	1.4440	37.48	36.61
$\text{CH}_2=\text{CHC}\equiv\text{C}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	76-77	60	0.7803	1.4571	42.66	41.23

Therefore, the complete analogy between the reaction of chloroprene with alkyl hypiodites and that of its homologs with alkyl hypoxidites was shown by the results of this investigation.

EXPERIMENTAL

I. Preparation of Alkylvinylacetylenes

40 g of powdered sodium amide was dissolved with efficient stirring in 1 liter of liquid ammonia over a 6-8 hr. period; gaseous vinylacetylene (100 ml of the liquid vinylacetylene, 25% excess) was then passed into the solution over a 6-8 hour period. The corresponding alkyl bromide (1 mole) was added drop wise (methyl bromide) was passed in as a gas) over 8-10 hours through a tube going to the bottom of the flask into the sodium vinylacetylide solution obtained. At the end of the reaction, the mixture was allowed to stand in order to evaporate the ammonia, whereby the alkylvinylacetylene which was distilling with the ammonia was condensed in absorbers filled with water and cooled with snow. The residue in the flask was treated with the ammonia solution from the absorption bottles, the oily layer collected in the absorption apparatus was added to it, and the mixture distilled. The lighter layer collected in the receiver, cooled with ice, over the ammonia water, was separated, washed 2 times with water, and dilute HCl solution, and distilled through a dephlegmator. Constants of the 7 substances obtained are given in Table 5.

The yield of the methyl homolog was 40-45% of theory, the ethyl about 50%, the propyl 80%, butyl 80% isomyl 70%.

TABLE 3

Substance	B.p., °C (85 mm)	d_4^{20}	n_D^{20}	MR _D	
				Found	Calculated
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH}_2$	58.5-59.5	1.0579	1.4712	31.34	30.86
$\text{CH}_2=\text{C}(\text{OC}_2\text{H}_5)\text{-CCl}=\text{CH}_2$	74.5-75	1.0204	1.4641	35.86	35.48
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH-CH}_3$	85-86	1.0322	1.4798	36.23	35.48
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH-C}_2\text{H}_5$	102-103.5	1.0179	1.4795	40.86	40.10
$\text{CH}_2=\text{C}(\text{OC}_2\text{H}_5)\text{-CCl}=\text{CH-C}_2\text{H}_5$	113.5-114.5	0.9875	1.4700	45.45	44.72
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH-C}_3\text{H}_7$	119-120	0.9566	1.4790	45.71	44.72
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH-C}_4\text{H}_9$	137.5-139.5	0.9833	1.4778	50.27	49.33
$\text{CH}_2=\text{C}(\text{OCH}_3)\text{-CCl}=\text{CH-CH(CH}_3)_2$	146-147	0.9684	1.4738	54.74	53.95
$\text{CH}_2=\text{C}(\text{OC}_2\text{H}_5)\text{-CCl}=\text{CH-CH(CH}_3)_2$	158-161	0.9656	1.4732	58.92	58.57

from chloroprene.

It is apparent from the data in Table 2 that the boiling point rises, and the density and refractive index decreases regularly in the homologous series of these ethers. All ethers have a specific odor (senna), are insoluble in water, and color upon storage as a result of the separation of iodine.

Hydrogen iodide is readily cleaved by the action of alkalis to form chloroalkoxyprene homologs. The physical properties of the substances obtained are compared in Table 3 with those of the previously obtained chloroalkoxyprenes.

It is apparent from the data in Table 3, that all of the substances boiled within a 1-3° range, and evidently, are a mixture of cis and trans isomers. Just as with the iodo ethers series, a regular rise in boiling point and decrease of density and refractive index occurs. All of the substances show an exaltation of about 0.5-0.9 units in the molar refractivity. The freshly prepared substances are colorless; they turn yellow and tar, and are transformed into viscous products. However, they are more stable than the chloroalkoxyprenes.

All of the ethers obtained are saponified to the corresponding ketones by dilute acids according to the equation:



The rate of saponification drops strongly in the homologous series. The ether with an isoamyl radical does not saponify completely after shaking for 10 hours with 5% H_2SO_4 at 40-50°.

The properties of the ketones obtained in this manner are given in Table 4, as well as those of the ketone obtained from chloroprene.

It is apparent from the data of Table 4 that the usual generalizations are found in the homologous series of these substances. All of the substances exhibit exaltation in the molecular refractivity.

Bromination, reduction, and formation of hydrazone were investigated from among the chemical properties of these ketones. All of the ketones readily brominate in chloroform solution with bromine; however, only the bromination product of the first ketone could be distilled. The rest of the substances decomposed upon distillation, forming hydrogen bromide. The reduction of these bromides with zinc proceeds with separation of hydrogen bromide, as a result of which a mixture of saturated and unsaturated ketones was obtained. The corresponding product from chloroprene was smoothly reduced to methyl ethyl ketone under these conditions.

The reduction of unsaturated chloroketones with colloidal platinum could not be realized because of the systematic poisoning of the catalyst.

The rate of semicarbazone formation decreases sharply with the increase in the size of the radical. p-nitrophenylhydrazones are formed readily upon heating; the semicarbazones are greatly affected for this reason, their melting points are not sharp, the 2,4-dinitrophenyl hydrazones melt more sharply.

TABLE 2

Substance	B.p. (°C) (10 mm)	d_4^{20}	n_D^{20}	MR _D	
				Found	Calculated
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}_2$	76.5-77	1.7135	1.5312	44.53	44.13
$\text{CH}_2=\text{CH}(\text{OC}_2\text{H}_5)\text{CCl}=\text{CH}_2$	82-83	1.6163	1.5220	49.16	48.75
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}-\text{CH}_3$	93.5-94.5	1.6355	1.5290	49.13	48.75
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	104-106	1.5267	1.5172	54.42	53.37
$\text{CH}_2=\text{CH}(\text{OC}_2\text{H}_5)\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	107-109	1.4687	1.5100	58.76	57.99
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}-\text{C}_3\text{H}_7$	115-117	1.4868	1.5163	58.68	57.99
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}-\text{C}_4\text{H}_9$	129-133	1.4293	1.5120	63.53	62.60
$\text{CH}_2=\text{CH}(\text{OCH}_3)\text{CCl}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	137-129	1.3930	1.5092	67.86	67.22
$\text{CH}_2=\text{CH}(\text{OC}_2\text{H}_5)\text{CCl}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	141-144	1.3436	1.5040	72.60	71.84

Iodoalkoxylation of chloroprene homologs was effected by the action of iodine and mercuric oxides upon their solutions in methyl and in several cases, ethyl alcohol.

The following 6 substances could have been expected as a result of the reaction, of which II and IV were the least probable, since they have never been found in reactions of conjugated systems.

I. $\text{CH}_2=\text{CH}(\text{OR})\text{CCl}=\text{CH}-\text{R}$; II. $\text{CH}_2(\text{OR})\text{CH}=\text{CCl}=\text{CH}-\text{R}$; III. $\text{CH}_2=\text{CH}-\text{CCl}(\text{OR})\text{CH}=\text{R}$;
IV. $\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}(\text{OR})-\text{R}$; V. $\text{CH}_2=\text{CH}=\text{CCl}-\text{CH}(\text{OR})-\text{R}$; VI. $\text{CH}_2(\text{OR})\text{CH}=\text{CCl}-\text{CH}=\text{R}$.

The structure of the main parts of the reaction products was proved in the following manner:

1) Propionic acid was obtained by the oxidation of the iodo ether of the chlorohexadiene by a neutral potassium permanganate solution, whereas iodoacetic acid was not present in any quantity in the reaction products. These results forced formulae III, IV, V, and VI to be discarded.

2) Dienic chloroether were obtained from all of the iodoethers by the action of alcoholic alkali, which could be hydrolyzed to unsaturated chloroketones by shaking with dilute acid solutions. Therefore, the chloroethers were derivatives of the enol forms of these ketones. These results forced formulae II, III, V, and VI to be discarded. Substances with formula II should have given unsaturated chloroaldehydes with these transformations; substances with formula III, an unsaturated iodo ketone or the acetal of the ketone; and finally, substances with formulae V and VI, ethers of unsaturated chloroalcohols. None of the possible reaction products were detected in any sort of a quantity.

Therefore, the iodoethers obtained must be assigned formula I.

Small lower and higher boiling fractions were always obtained in addition to the main substance during the iodoalkoxylation of the chloroprene homologs. They arose, to a great extent, as a result of the fairly strong decomposition of the iodo ethers during distillation. 1,4-Products could be found in the higher boiling fraction, but their quantity was small. If half of the whole residue after separation of the main substance was assigned to the 1,4 products, then their yield would not exceed one tenth that of the main substance. In most cases, it was considerably below this value.

Therefore, it was shown that alkyl hypodites add to chloroprene homologs in the same order as to chloroprene.

The physical properties of the ethers are given in Table 2 along with the corresponding properties of the ethers

TABLE 8

Substance	Weight of sample (g)	Weight AgCl (g)	% Cl	
			Found	Calculated
$\text{CH}_2=\text{C}(\text{OCH}_3)-\text{CCl}=\text{CH}-\text{CH}_3$	0.1199	0.1298	26.78	26.74
	0.1028	0.1120	26.95	26.74
$\text{CH}_2=\text{C}(\text{OCH}_3)-\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	0.1128	0.1104	24.21	24.18
$\text{CH}_2=\text{C}(\text{OC}_2\text{H}_5)-\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	0.1234	0.1084	21.73	22.07
$\text{CH}_2=\text{C}(\text{OCH}_3)-\text{CCl}=\text{CH}-\text{C}_3\text{H}_7$	0.1004	0.0880	21.68	22.07
$\text{CH}_2=\text{C}(\text{OCH}_3)-\text{CCl}=\text{CH}-\text{C}_4\text{H}_9$	0.1176	0.0961	20.22	20.30
	0.1157	0.0940	20.10	20.30
$\text{CH}_2=\text{C}(\text{OCH}_3)-\text{CCl}=\text{CH}-(\text{CH}_2)_2-\text{CH}(\text{CH}_3)_2$..	0.1054	0.0786	18.45	18.79
	0.1212	0.0892	18.22	18.79
$\text{CH}_2=\text{C}(\text{OC}_2\text{H}_5)-\text{CCl}=\text{CH}-(\text{CH}_2)_2-\text{CH}(\text{CH}_3)_2$..	0.1282	0.0914	17.64	17.49

TABLE 9

Substance	Weight of sample (g)	Weight AgCl (g)	% Cl	
			Found	Calculated
$\text{CH}_3-\text{CO}-\text{CCl}=\text{CH}-\text{CH}_3$	0.1380	0.1630	29.22	29.90
	0.1156	0.1383	29.60	29.90
$\text{CH}_3-\text{CO}-\text{CCl}=\text{CH}-\text{C}_2\text{H}_5$	0.1214	0.1289	26.27	26.75
$\text{CH}_3-\text{CO}-\text{CCl}=\text{CH}-\text{C}_3\text{H}_7$	0.1339	0.1296	23.94	24.18
	0.0974	0.0942	23.92	24.18
$\text{CH}_3-\text{CO}-\text{CCl}=\text{CH}-\text{C}_4\text{H}_9$	0.1224	0.1072	21.66	22.07
	0.1285	0.1108	21.33	22.07
$\text{CH}_3-\text{CO}-\text{CCl}=\text{CH}-(\text{CH}_2)_2-\text{CH}(\text{CH}_3)_2$	0.1378	0.1064	19.10	20.30

By bromination of the ketones with the theoretical amount of bromine in chloroform, their bromides were obtained, of which only 1 could be distilled; the rest decomposed with the evolution of hydrogen bromide. Upon reducing them with zinc shavings in 80% acetic acid, in several cases mixtures of saturated and unsaturated ketones were obtained, whose separation into components was not attempted. The chlorobromo ketones were not oxidized in the cold with chromic mixture; this led to the conclusion that they did not contain aldehydes as impurities.

SUMMARY

1. The order of addition of alkyl hypiodites to homologs of chloroprene was investigated, and several of these homologs were first synthesized.
2. It was shown that alkyl hypiodites added in the same order as to chloroprene, predominantly to the unsubstituted double bond.
3. A series of dienic chloroethers was obtained by the action of alcoholic alkalis upon the chloroethers: 2-methoxy-3-chloropentadiene-1,3, 2-methoxy-3-chlorohexadiene-1,3, 2-ethoxy-3-chlorohexadiene-1,3, and others.
4. A series of methylchlorovinyl ketones was obtained by hydrolytic cleavage of these ethers. 3-Chloropenten-3-one-2, 3-chlorohexen-3-one-2, and others.

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Received January 31, 1953

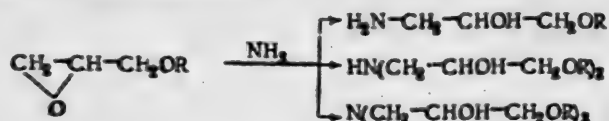
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REACTIONS OF ETHER OXIDES WITH NITROGEN COMPOUNDS

VI. REACTION OF METHYL AND ETHYL GLYCIDE ETHERS WITH DIETHYLAMINE

F. G. Ponomarev

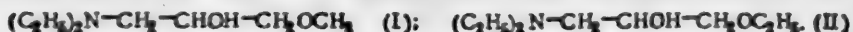
In the previous communication [1] it was shown that methyl and ethyl glycidic ethers reacted quite energetically with ammonia (in contrast to amides) [2-4] even at room temperature with the formation of the corresponding ethers of aminopropanediol:



The present communication reports the results of experiments on the reaction of methyl and ethyl glycidic ethers with diethylamine.

The reaction of methyl glycidic ether with diethylamine has not been reported in the literature, while the reaction of ethyl glycidic ether with secondary amines is only mentioned slightly [5].

Experiments showed that glycidic ethers react readily with aqueous solutions of diethylamine to form the expected ethers of diethylaminopropanediol:



In the absence of water, these substances do not noticeably react at usual or elevated (80°) temperatures.

Heating greatly accelerates the reaction with the aqueous amine so that the yield of the diethylaminopropanediol ethers is only slightly smaller after a 3 hour heating on the boiling water bath than after 72 hours standing at room temperature. Further increase of the temperature to 125-130° and of the heating time to 6 hours did not give better results.

The reagents were taken in a ratio of 1 mole of the ether to 2 or 3 moles of diethylamine. Under these conditions the reaction proceeded only in the direction of the formation of aminopropanediol ethers (I) and (II), and is not accompanied by side processes. The reaction with glycidic ethers proceeds at approximately the same rate as with propylene oxide [6] and considerably greater than with trimethylethyl oxide [7].

Ethers of aminopropanediol (I) and (II) which were obtained are colorless liquids with basic properties, less hygroscopic than the corresponding products obtained by the reaction of the same ethers with ammonia [1].

The presence of hydroxyl groups in the aminoalcohols (I) and (II) was proved by acetylation with acetic anhydride. Acetates were obtained from both bases, and in addition, an ethiodide was obtained for amine (I).

EXPERIMENTAL

Glycidic ethers were obtained from glycerine α -monochlorohydrin ethers [8-15]. 1.2 mole of powdered potassium hydroxide, 250 ml of absolute ether, were placed into a round-bottom flask with a reflux condenser, and 1 mole of purified glycerine chlorohydrin was added over a 1.5 hour period through the condenser in small portions with shaking. A slight heating occurred. The mixture was heated for 1 hour to 50-60° on the water bath, the residue was then separated, washed with 3 times with 30 ml of dry ether, the ether was removed on the water bath, and the product distilled through a three ball dephlegmator. The yield of glycidic methyl ether was 65%, the ethyl, 62%.

Reaction of Glycidic Methyl Ether with Diethylamine. Synthesis of 3-methoxypropanol-2-diethylamine (I) (together with E. F. Parinova).

a) 37 g (0.5 moles) of diethylamine (b.p. 56-57°) in 75 ml of water was added with shaking to 15 g (0.17

mole) of glycidic methyl ether (b.p. 110-112°, n_D^{25} 1.4042). A homogenous colorless liquid was obtained upon mixing the reagents, and the temperature rose from 20-60° (if the mixture was not cooled with water).

After heating the mixture for 3 hours on the boiling water bath, the amino alcohol formed was salted out with potassium hydroxide, separated (upper layer), dried with KOH, and vacuum distilled. 21.5 g (78.4%) of 3-methoxypropanol-2-diethylamine (I) was obtained. The yield here and subsequently was calculated on the basis of the glycidic ether.

In two other analogous experiments in which the heating was continued for 5 hours at 125-130° on the oil bath, 65 and 68% of product (I) was obtained.

b) 68.5 g (0.9 mole) of diethylamine in 134 ml of water was added to 29.2 g (0.33 mole) of the methyl ether, and the mixture allowed to stand at room temperature for 72 hours. As a result of the processing of the product analogously to the previous experiment, 30.9 g (52%) of the aminopropanediol ether (I) was obtained. If the amount of 33% amine was decreased from three to two moles per mole of ether, and the time of standing from 72 to 66 hours, the yield of the product fell to 44%.

3-Methoxypropanol-2-diethylamine had the following constants after redistillation in vacuum:

B.p. 75-77° at 6 mm; d_4^{25} 0.9221; n_D^{25} 1.4390; M_R 45.95; calculated 46.25.

0.1449 g substance: 8.86 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1272 g substance: 7.72 ml 0.1 N H_2SO_4 . 0.1410 g substance: 0.2034 g AgI (according to Ziesel). 0.1968 g substance: 11.81 ml 0.1 N NaOH. 0.3470 g substance: 26.48 g benzene: Δ 0.41°. 0.4370 g substance: 26.48 g benzene: Δ 0.52°. Found %: N 8.56, 8.49; CH_3O 19.04; OH 10.19; M 163.02, 161.9. $C_8H_{19}O_2N$. Calculated %: N 8.69; CH_3O 19.24; OH 10.54; M 161.2.

The aminoalcohol ether obtained was a colorless liquid with a weak amine odor, which allowed slightly upon standing. It did not distill at atmospheric pressure without decomposition. It was slightly soluble in alcohol, ether, and dioxane, poorly in cold, and more so in hot water. It rapidly decolorized a carbon tetrachloride solution of bromine and potassium permanganate. It reacted with metallic sodium. It kept unchanged for a long time in closed vessels. It absorbed moisture under usual conditions in the air. A sample of 0.9718 g gave a weight increase of 1.6% after 6 hours.

The picrate of this aminoalcohol, obtained by mixing equimolecular amounts of alcoholic solutions of the base and picric acid, was a lemon yellow crystalline substance which melted at 162° after two recrystallizations from water. The picrate was analyzed in the manner reported previously [1].

0.1020 g substance: 10.1 ml 0.1 N H_2SO_4 . 0.1131 g substance: 11.23 ml 0.1 N H_2SO_4 . Found %: N 13.86, 13.90. $C_{14}H_{21}O_5N_4$. Calculated %: N 14.35.

The ethiodide of base (I) was obtained by mixing solutions of equimolecular amounts of the reagents in absolute ether. Washed many times with ether, the ethiodide melted at 96-97°. Colorless crystals, readily soluble in water and alcohol.

0.1942 g substance: 6.11 ml 0.1 N $AgNO_3$. 0.1168 g substance: 3.70 ml 0.1 N $AgNO_3$. 0.1578 g substance: 4.94 ml 0.1 N H_2SO_4 . 0.1440 g substance: 4.44 ml 0.1 N H_2SO_4 . Found %: I 39.93, 40.20; N 4.38, 4.31. $C_{11}H_{24}O_2NI$. Calculated %: I 40.01; N 4.41.

The aminoalcohol hydrochloride was obtained by the evaporation of a solution of the product in dilute hydrochloric acid on the water bath, and was a viscous, noncrystallizing mass.

The aminoalcohol acetate was obtained by the action of acetic anhydride on the propanediol ether (I) in the presence of a drop of sulfuric acid. It was a colorless liquid with a specific odor.

B.p. 82-84° at 8 mm; d_4^{25} 0.9817; n_D^{25} 1.4340; M_R 54.10; calculated 55.61. 0.1376 g substance: 6.78 ml 0.1 N H_2SO_4 . 0.1211 g substance: 6.04 ml 0.1 N H_2SO_4 . Found %: N 6.89, 6.98; $C_{12}H_{21}O_3N$. Calculated %: N 6.89.

The acetate was readily soluble in water, alcohol, and insoluble in benzene.

The aminoalcohol (I) obtained did not give a crystalline derivative with gold chloride.

Reaction of Glycidic Ethyl Ether with Diethylamine. Synthesis of 3-Ethoxypropanol-2-diethylamine (II)
(together with A. V. Zlobina)

a) 36.5 g of freshly distilled diethylamine was added to 17 g (~0.17 mole) of glycidic ethyl ether (b.p. 124-126°, n_D^{20} 1.4080). Heating occurred upon mixing (the temperature rose from 18-65°). When heated on the boiling water bath, the reaction mixture was first homogenous, and then separated into two layers after 15-20 minutes. The upper, which was the aminoalcohol (II), was separated after heating for 3 hours, another small layer was formed by saturating the water solution with potassium hydroxide (KOH), which was combined with the initially separated one, dried with solid potassium hydroxide, and was vacuum distilled. 24 g (80%) of 3-ethoxypropanol-2-diethylamine (II) was obtained.

In two analogous experiments, but with heating on an oil bath at 125-130°, 62.9% of the reaction product was obtained by a 5 hour heating, and 56% after 1 hour heating.

b) 33.6 g (0.46 mole) of diethylamine in 69 ml of water was added to 23.5 g (0.23 mole) of the ether, and the mixture was allowed to stand at room temperature for 72 hours. After the corresponding processing and vacuum distillation, 22.9 g (57%) of 3-ethoxypropanol-2-diethylamine was obtained. This aminoalcohol was obtained in a yield of 48% of theory as a result of 2 hours standing at room temperature and an initial energetic 30 minute shaking.

The 3-ethoxypropanol-2-diethylamine obtained had the following constants after redistillation:

B.p. 84-85° at 6 mm; d_4^{20} 0.9100; n_D^{20} 1.4390; MR_D 50.25; calculated 50.87.

0.1003 g substance: 5.69 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1198 g substance: 6.03 ml 0.1 N H_2SO_4 . 0.1961 g substance: 0.2597 g AgI (according to Zeisel). 0.1882 g substance: 10.25 ml 0.1 N NaOH. 0.1074 g substance: 22.82 g benzene: Δt 0.17°. 0.1152 g substance: 22.82 g benzene: Δt 0.126°. Found %: N 7.99, 7.88; $C_8H_{19}O$ 25.40; OH 9.26; M_{av} 174.7. $C_8H_{19}O_2N$. Calculated %: N 7.99; $C_8H_{19}O$ 25.70; OH 9.70; M 175.26.

The colorless liquid with a weak odor of amine, which yellowed slightly on standing, had an alkaline reaction and a bitter burning taste. It did not distill at ordinary pressure without decomposition. It was readily soluble in alcohol, ether, and dioxane, poorly, in cold and more so in hot water. It rapidly decolorized a chloroform solution of bromine and a potassium permanganate solution, reacted with metallic sodium. It absorbed moisture under the usual conditions. A sample of 0.9763 g of the substance gave weight increase of 1.5% after 6 hours.

The picrate of the aminoalcohol was a light yellow crystalline substance with m.p. 83° (from water).

0.1203 g substance: 11.03 ml 0.1 N H_2SO_4 . 0.1152 g substance: 10.41 ml 0.1 N H_2SO_4 . Found %: N 12.84, 12.65. $C_{15}H_{24}O_7N_4$. Calculated %: N 13.85.

The picrate contained less nitrogen than required by theory. Apparently, it crystallized with two molecules of water which were stably held and were not given off even upon prolonged standing in a desiccator over H_2SO_4 and upon heating in a drying cabinet at 80-90°.

The ethiodide of the base precipitated in the form of a non-crystallizing oil.

The chloroaurate of the base gave a lower percent of gold upon analysis. It could not be purified any further.

The acetate of the aminoalcohol, obtained under the same conditions as the acetate of aminoalcohol (I), was a colorless liquid with a specific odor; it was readily soluble in water, alcohol, and ether.

B.p. 95-97° at 8 mm; d_4^{20} 0.9420; n_D^{20} 1.4370; MR_D 60.39; calculated 60.24. 0.1165 g substance: 4.50 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1062 g substance: 4.16 ml 0.1 N H_2SO_4 . Found %: N 5.41, 5.48. $C_{11}H_{23}O_3N$. Calculated %: N 6.44.

The acetate was not completely pure and contained a lower percent of nitrogen than required by theory. It could not be purified any further.

SUMMARY

1. The reaction of glycidic methyl and ethyl ethers with aqueous diethylamine was studied.
2. The following products of these reactions were obtained and characterized: 3-methoxypropanol-2-diethylamine, 3-ethoxypropanol-2-diethylamine, their acetates and several salts.

3. It was shown that glycidic ether resembles propylene oxide in activity and reaction with diethylamine, and are considerably more active than trimethylethylene oxide.

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Received December 23, 1962

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- * See Consultants Bureau Translation, p. 681.
- ** See Consultants Bureau Translation, p. 2135.
- *** See Consultants Bureau Translation, p. 151.
- **** See Consultants Bureau Translation, p. 985.

CONDENSATION PRODUCTS OF TRIARYLCARBINOL WITH 1-PHENYL-3-METHYLPYRAZOLONE-5

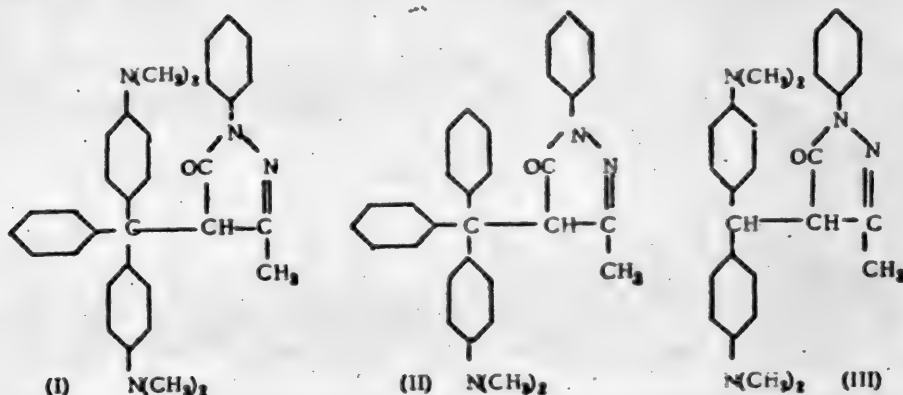
O. F. Ginzburg and V. R. Ter-hk'n

As is known, triphenylcarbinol possesses a very labile hydroxyl group, and its basic properties are expressed to a considerable extent [1]. The basic properties are expressed to a greater extent in derivatives of triphenylcarbinol containing a substituent of the primary type in the para position to the central carbon atom. Especially active are the hydroxyl groups in carbinol compounds obtained from the basic triphenylmethane dyes, which is expressed, in particular, in reaction of these substances with compounds containing labile hydrogen atoms and methyl and methylene groups. It is known, for example, that triphenylcarbinol itself reacts with malonic ester to form triphenylmethylmalonic ester [2]. Recently, A. N. Nesmeyanov and coworkers showed that 4,4',4"-hexamethylaminotriphenylcarbinol or its methyl ether participates in a condensation reaction with nitromethane and aliphatic aldehydes to form compounds in which the tris(dimethylaminophenyl)methyl radical bound to the aldehyde or nitromethane residue is very labile [3].

In the present investigation, it was decided to examine the ability of several carbinol compounds and their methyl ethers to participate in condensation reactions with 1-phenyl-3-methylpyrazolone-5 which, as is known, contains very active hydrogen atoms.

The experiments conducted showed that 4,4'-tetramethyldiaminodiphenylcarbinol, 4,4'-tetramethyldiaminotriphenylcarbinol, and its methyl ether, as well as 4-dimethylaminotriphenylcarbinol methyl ether readily participate in condensation reactions with 1-phenyl-3-methylpyrazolone-5. Thus, for example, even upon heating the above compounds with 1-phenyl-3-methylpyrazolone-5 in methyl alcohol, lightly colored condensation products are formed which gradually precipitate from the solution. Upon heating 4,4',4"-hexamethylaminotriphenylcarbinol with 1-phenyl-3-methylpyrazolone-5 in methyl alcohol, only an intensely violet colored solution forms from which, however, the reaction product does not precipitate.

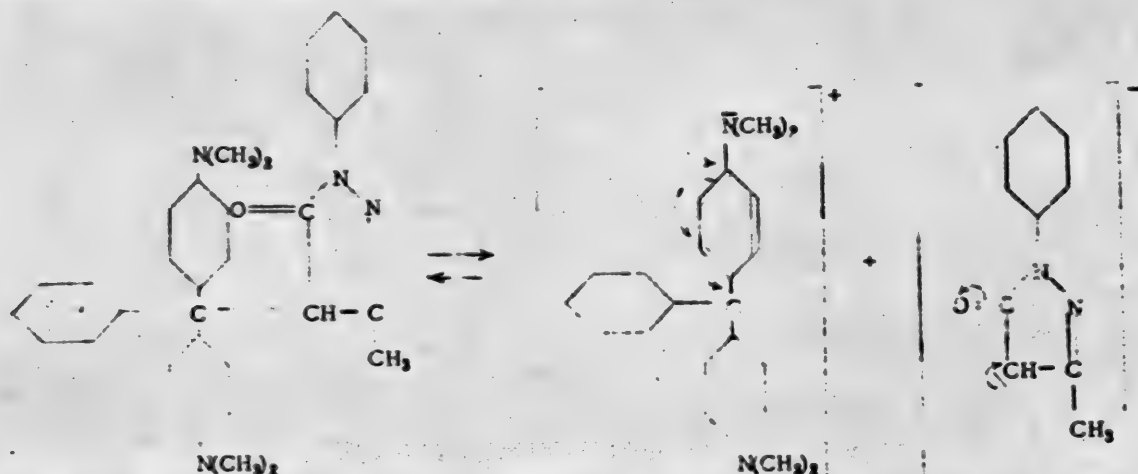
A study of the properties, as well as the analysis of the products obtained showed that these substances possess the following structures:



It must be mentioned that, under the above conditions, triphenylcarbinol does not participate in a condensation reaction with 1-phenyl-3-methylpyrazolone-5 because of the insufficient basicity of triphenylcarbinol.

The compounds synthesized have the ability to dissolve in aqueous alcoholic alkali solutions because of the presence of the 1-phenyl-3-methylpyrazolone-5 residue in them, from which they are precipitated by careful acidification with acetic acid. These compounds, like the products of the condensation of 4,4',4"-hexamethylaminotriphenylcarbinol with aliphatic aldehydes and nitromethane, reported by A. N. Nesmeyanov and coworkers [3], are subjected to acidolysis. Thus for example, solutions of the color of the corresponding dye are formed by the action of acetic acid. However, the decomposition of these compounds also occurs upon solution in certain aprotic polar solvents.

Thus for example, a solution of color corresponding to the dye is formed by dissolving compounds (II) and (III) in nitrobenzene, while compound (I) decomposes not only in nitrobenzene, but also in chloro- and bromobenzene. As an example, absorption spectra of malachite green and compound (I) in nitrobenzene are given in Fig. 1. Comparison of these absorption curves shows their identity. Thus, since the color of solutions of malachite green is caused by the presence of cations of the dye, therefore, compound (I) has these same cations in nitrobenzene. The dissociation of compounds (I), (II), and (III) into ions occurs in the same manner in a series of polar solvents, and the dissociation, for example, of compound (I) may be described by the following equations:



More detailed study of nitrobenzene solutions of compounds (I) and (II) showed that the dissociation of these compounds is not complete. The degree of dissociation of compound (I) in nitrobenzene was calculated by the determination of the concentration of dye cations in the nitrobenzene solution of known concentration of compound (I) from the intensity of absorption. Measurement of the intensity of absorption of the same nitrobenzene solution of compound (I) at various intermediate times showed that its dissociation in nitrobenzene proceeds comparatively slowly. Data characterizing the change of the degree of dissociation with time of compound (I) in nitrobenzene solution is given below, where the time is given from the moment of the first measurement.

TABLE 1

Change of the Degree of Dissociation of Compound (I)

Degree of dissociation	Time (in minutes)											
	00	30	57	89	119	149	180	209	239	279	300	1202
α %	3.83	5.30	6.11	7.76	8.56	9.73	11.0	11.9	13.1	13.5	14.0	19.4

The same picture is also found upon the study of the dissociation of Compound (II) in nitrobenzene. It must be mentioned that the dissociation of compound (II) proceeds considerably more slowly than that of compound (I) (Fig. 2). Since the accumulation of colored cation in the nitrobenzene solutions decreases gradually in both cases, it must be supposed that finally, an equilibrium between the dissociated and undissociated parts of compounds (I) and (II) is reached in the solution.

EXPERIMENTAL

1. 4,4'-Tetramethyldiaminotriphenyl-(1-phenyl-3-methylpyrazolone-5-yl-4)methane (compound I)

a) 5.06 g of 4,4'-tetramethyldiaminotriphenylcarbinol methyl ether was added to a solution of 7.50 g of 1-phenyl-3-methylpyrazolone-5 in 40 ml of methyl alcohol, and the mixture was refluxed for 4 hours in a flask. After cooling, the precipitate was filtered, thoroughly washed with alcohol and benzene, and dried in a vacuum desiccator over potassium hydroxide. The compound obtained melted with decomposition at 162-165°. Yield 6.37 g or 91.4% of the theoretical based on malachite green methyl ether.

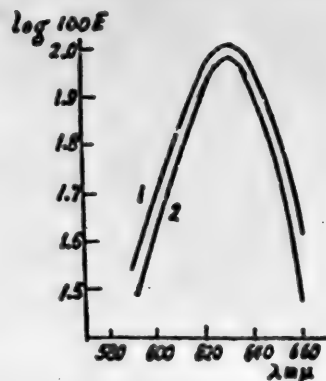


Fig. 1. Absorption spectra of malachite green hydriodide and compound (I).

1) The hydriodide; 2) compound (I).

TABLE 2

c · 10 ⁶ moles/liter	E	K · 10 ⁻⁵
0.50	0.4007	1.60
1.25	1.0069	1.61

TABLE 4

c · 10 ⁶ moles/liter	E	K · 10 ⁻⁴
3.45	0.4204	2.44
4.32	0.5040	2.50
5.18	0.6430	2.48
6.05	0.7528	2.50
6.90	0.9020	2.62
8.35	1.0201	2.44
8.64	1.1093	2.58

TABLE 3

Time (min.)	E	Cation conc. x · 10 ⁶ moles/liter	α %
00	0.2495	5.305	3.83
30	0.3408	0.424	5.30
57	0.3934	0.489	5.7
89	0.4998	0.620	7.78
119	0.5918	0.686	8.56
149	0.6252	0.778	9.73
180	0.7097	0.884	10.99
209	0.7636	0.949	11.87
239	0.8412	1.046	13.09
279	0.8730	1.086	13.59
300	0.8997	1.119	13.88
1202	1.2447	1.550	19.40

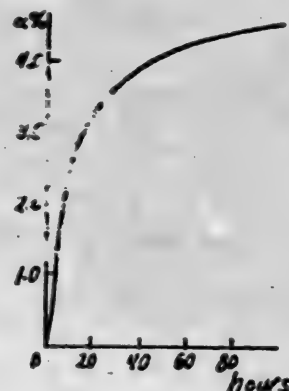


Fig. 2 Change of the degree of dissociation. (of II).

b) 0.5 g of 4,4'-tetramethyldiaminotriphenylcarbinol was added to a solution of 0.75 g of 1-phenyl-3-methylpyrazolone-5 in 20 ml of methyl alcohol. The solution obtained was refluxed for 2 hours. After cooling the precipitate was filtered, thoroughly washed with alcohol and benzene, and dried in a drying chamber at 80°. The compound obtained melted with decomposition at 162-165°. Yield 0.46 g or 66.3% of the theoretical based on 4,4'-tetramethyldiaminotriphenylcarbinol.

0.1424 g substance: 0.4105 g CO₂; 0.0905 g H₂O. 0.0637 g substance: 6.20 ml N₂ (22°, 761 mm).

0.0778 g substance: 7.81 ml N₂ (24°, 758 mm). Found %: C 78.62; H 7.11; N 11.20, 11.40.

C₂₃H₂₄ON₄. Calculated %: C 78.84; H 6.82; N 11.14.

Determination of the absorption coefficient of a nitrobenzene solution of malachite green hydroiodide. All of the spectrophotometric measurements were effected on the Koenig-Martens spectrophotometer. Malachite green hydroiodide was prepared by the decomposition of 4,4'-tetramethyldiaminotriphenylcarbinol methyl ether with methyl magnesium iodide. A solution of malachite green hydroiodide in nitrobenzene was prepared and intensity of absorption E of these solutions at λ = 630 mμ and 5 cm layer thickness was measured. The absorption coefficient was calculated on the basis of the data obtained (Table 2).

Determination of the degree of dissociation of 4,4'-tetramethyldiaminotriphenyl-(1-phenyl-3-methylpyrazolone-5-yl-4)-methane in nitrobenzene. A sample of compound (I) was ground with a small amount of nitrobenzene, and the mixture was washed into a 50 ml volumetric flask. The contents of the flask were shaken until complete solution of compound (I), and the solution was brought to the mark; then a solution was prepared by subsequent dilution the concentration of which was 8 · 10⁻⁶ moles/liter. The intensity of absorption of the solution was measured periodically at λ = 630 mμ, and 5 cm layer thickness. The recording of the time is given from the moment of the first measurement. The solution was kept at 21 ± 0.5°. The absorption coefficient from the data of Table 2 was taken to be equal to 1.60 · 10⁵. The results obtained are given in Table 3.

II. 4-Dimethylaminotriphenyl-(1-phenyl-3-methylpyrazolone-5-yl-4)-methane (Compound II)

2.30 g of 4-dimethylaminotriphenylcarbinol methyl ether was added to a solution of 1.27 g of 1-phenyl-3-methylpyrazolone-5 in 50 ml of methyl alcohol, and the mixture obtained was refluxed for 6 hours in a flask. The solution was colored red, and a voluminous precipitate formed at the end of the heating. On the following day, the residue was filtered, thoroughly washed with alcohol and benzene, and dried in a drying cabinet at 85°. 2.61 g of a product with m.p. 179-180° was obtained. Yield 77.5% of the theoretical based on the starting methyl ether of 4-dimethylaminotriphenylcarbinol.

0.1402 g substance: 0.4147 g CO₂; 0.0824 g H₂O. 0.0899 g substance: 7.40 ml N₂ (21°, 757 mm).

0.0698 g substance: 5.86 ml N₂ (22°, 763 mm). Found %: C 80.67; H 6.57; N 9.46, 9.64. C₂₃H₂₄ON₂.

Calculated: C 81.00; H 6.36; N 9.48.

TABLE 5

Time (min.)	E	Cation conc. $\times 10^4$ moles/liter	α %
0.0	0.4519	3.65	0.20
0.5	0.5583	4.50	0.25
1.2	0.7618	6.15	0.34
1.8	0.9531	7.69	0.42
2.5	1.2613	10.30	0.57
31.0	0.9363*	67.5	3.73
55.0	0.9602*	77.5	4.29
101.0	1.0291*	82.6	4.56

benzene, and the mixture washed into a volumetric flask. The contents of the flask were shaken until complete solution of the compound (II). A solution was prepared by subsequent dilution, whose concentration was equal to $1.81 \cdot 10^{-3}$ moles/liter. The preparation of the solution was effected in red light. The intensity of absorption was measured periodically at $\lambda = 500 \text{ m}\mu$ and 5 cm layer thickness. The recording of the time was started from the moment of the first measurement. The solution was kept at $21 \pm 0.5^\circ$. The absorption constant was taken to be equal to $2.50 \cdot 10^4$ from the data in Table 4. The data obtained are given in Table 5.

III. 4,4'-Tetramethyldiaminodiphenyl-(1-phenyl-3-methylpyrazolone-5-yl-4)-methane (Compound III)

1.00 g of 4,4'-tetramethyldiaminodiphenylcarbinol and 0.68 g of 1-phenyl-3-methylpyrazolone-5 were dissolved in 30 ml of methyl alcohol. The solution was refluxed for 2 hours on the water bath in a flask. On the following day, the precipitate which formed was filtered, thoroughly washed with alcohol, and dried in a drying cabinet at 90° . The substance melted with decomposition at $193-194^\circ$. The melting point did not change after recrystallization from alcohol. The compound obtained was identical with 4,4'-tetramethyldiaminodiphenyl-(1-phenyl-3-methylpyrazolone-5-yl-4)-methane synthesized by Kehlhardt [4].

SUMMARY

The 4,4'-tetramethyldiaminodiphenylcarbinol, the methyl ether of the 4-tetramethyldiaminotriphenylcarbinol, the 4,4'-tetramethyldiaminotriphenylcarbinol, and its methyl ether condense readily with 1-phenyl-3-methylpyrazolone. When dissolved in polar solvents, the products of condensation dissociate into ions, and the cations formed are identical to those formed by the corresponding dyes dissolved in the same solvents.

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Received November 6, 1952.

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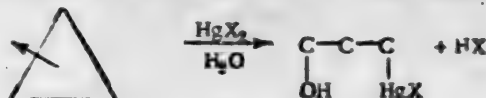
*Before the determination the solution is diluted 10 times.

REACTION OF CYCLOPROPANE HYDROCARBONS WITH SALTS OF MERCURIC OXIDE

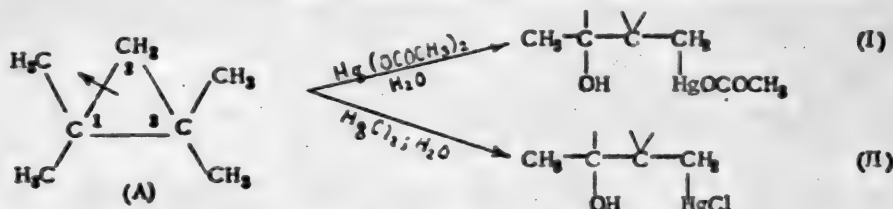
II. NEW ORGANO-MERCURY COMPOUNDS FROM 1,1,2,2-TETRAMETHYLCYCLOPROPANE

R. Ya. Levina and V. N. Kostin

In the previous communication [1] one of the authors (together with B. M. Gladshstein) disclosed the discovery of a reaction opening the three membered ring under the action of salts of mercuric oxide.

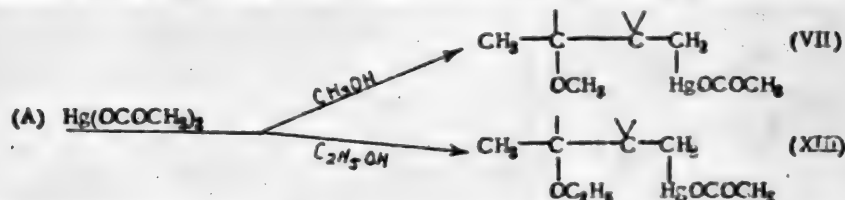


The reaction of 1,1,2,2-tetramethylcyclopropane (A) with mercuric acetate and chloride in aqueous solution was studied; a detailed investigation of the reaction products showed that the opening of the ring occurs between alkylated and the unalkylated carbon atoms (upon link 1,2) and leads to the formation of 3-hydroxy-2,2,3-trimethylbutyl-mercuric acetate (I) and 3-hydroxy-2,2,3-trimethylbutyl mercuric chloride (II) respectively:

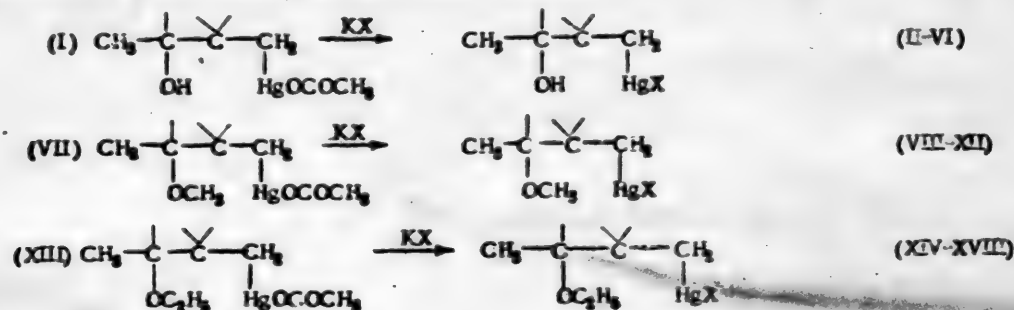


Therefore, this reaction is a method for the synthesis of a new type of compound, γ -mercurated alcohols, whose preparation can serve as a method of identification of the cyclopropane series of hydrocarbons.

In the present investigation, the method for the preparation of 3-hydroxy-2,2,3-trimethylbutyl mercuric acetate (I) was improved, and the corresponding methoxy and ethoxy compounds were obtained by the reaction between 1,1,2,2-tetramethylcyclopropane with mercuric acetate in methanol and ethanol: 3-methoxy-2,2,3-trimethylbutyl mercuric acetate (VII) and 3-ethoxy-2,2,3-trimethylbutyl mercuric acetate (XIII).

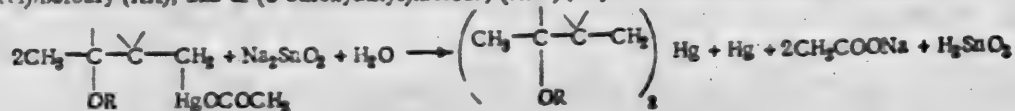


Each of the acetates obtained (I, VII, XIII) was transformed by the action of potassium chloride, bromide, iodide, cyanide, and thiocyanate (with cooling and using equimolecular amounts of the reacting substances) into the chloride, bromide, iodide, cyanide, and thiocyanate, respectively:



(where X = Cl, Br, I, CN, CNS).

The action of a symmetrical agent, an alkaline solution of sodium stannite, upon 3-hydroxy-, 3-methoxy-, and 3-ethoxyalkyl mercuric acetate resulted in the preparation of di-(3-hydroxyalkyl) mercury (XIX), di-(3-methoxyalkyl)mercury (XX), and di-(3-ethoxyalkyl)mercury (XXI) (alkyl = 2,2,3-trimethylbutyl), respectively.



(where R = H, CH₃, C₂H₅).

All of the organo-mercury compounds obtained are being reported for the first time, with the exception of (I) and (II) which were reported in the previous communication.

EXPERIMENTAL

1,1,2,2-Tetramethylcyclopropane (b.p. 75.2° at 750 mm, n_D^{20} 1.4003; d_4^{20} 0.7185) was obtained by a method previously developed by the authors [2] from 2,4-dimethylpentadiene-1,3.

Below are given methods for the preparation of the new organo-mercury compound from tetramethylcyclopropane; their yields, melting points, and analyses for the mercury content (and in isolated cases for carbon, hydrogen, and nitrogen) are given in the Table.

Preparation of 3-Hydroxy-2,2,3-trimethylbutyl Mercuric Acetate (I)

12.8 g of tetramethylcyclopropane was added to a filtered solution of 41.6 g of mercuric acetate in 150 ml of distilled water. The reaction mixture was left to stand for 6 days (in a closed bottle) at -5° with periodic shaking. At the end of the reaction (disappearance of the hydrocarbon layer and the absence of the mercuric salt in the solution), the organo-mercury compound partially separated in the form of coarse white crystals. The larger part of the water (4/5 of the volume) was vacuum distilled from the solution at 6 mm; the main mass of the crystals (not containing impurities of mercuric or mercurous salts according to the reaction with alkali and ammonia) came out of the residue upon cooling with ice, which was recrystallized from heptane.

3-Hydroxy-2,2,3-trimethylbutyl mercuric acetate was readily soluble in the cold in ether, acetic acid, chloroform, dioxane, and acetone.

Preparation of 3-Methoxy- and 3-Ethoxy-2,2,3-trimethylbutyl Mercuric Acetates (VII) and (XIII)

The reaction between tetramethylcyclopropane (6.6 g) and a solution mercuric acetate (20.8 g) in absolute methyl alcohol (200 ml), as well as in absolute ethyl alcohol (630 ml*), was effected with the same method used above for the preparation of preparation (I). The reaction time was 3 days. After the removal of the alcohol in vacuum from each reaction mixture, a viscous oil remained which was dissolved once more in absolute ether, the solution filtered, and the ether removed in a stream of nitrogen at reduced pressure. The oil obtained was dried in a desiccator over fused calcium chloride or phosphorus pentoxide.

The methoxy compound crystallized after standing for 2 days; the ethoxy compound was a non-crystalline viscous oil. Both compounds were readily soluble in ether.

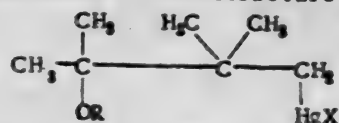
Substitution of the Acetate Group of 3-Hydroxy-, 3-Methoxy-, and 3-Ethoxy-2,2,3-trimethylbutyl Mercuric Acetate by a Chloride, Bromide, Iodide, and Cyanide and Thiocyanate Group [3]

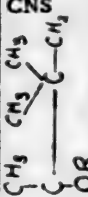
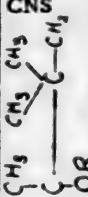
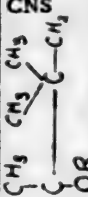
A cooled aqueous solution (20 ml) of an equimolecular amount of potassium chloride (0.75 g), or bromide (1.19 g), iodide (1.66 g), cyanide (0.65 g), and thiocyanate (0.97 g) was added gradually with continuous stirring to an ice cooled solution of 3-hydroxy-2,2,3-trimethylbutylmercuric acetate (3.74 g, 0.01 mole) in water (150 ml).

In all cases crystalline precipitates formed which were recrystallized from petroleum ether after washing with water and alcohol, and drying in a desiccator over calcium chloride. Since 3-methoxy- and 3-ethoxy-2,2,3-trimethylbutyl mercuric acetates were poorly soluble in water, the solutions of the potassium salts were added with continuous stirring to water emulsions (110-150 ml) of the methoxy- or the ethoxy-compound (0.01 mole); the reaction mixture was then stirred for 3-4 hours more. The 3-methoxy and 3-ethoxyalkyl mercuric salts obtained

* Mercuric acetate is less soluble in ethyl alcohol than in methyl.

Organo-Mercury Compounds of the Structure



Expt.	R	X	Substance (Alkyl = 2,2,3-trimethylbutyl)	M.p. (°C)	Yield (in % of the theoreti- cal)	Analysis			
						Weight of sample (g)	Hg(g)	Hg (in %)	
							Found	Calc.	
I	H	OCOCH ₃	3-Hydroxyalkyl mercuric acetate	66-70	64	0.3458	0.2154	53.71	53.55
II	H	Cl	" " chloride	110.-117	92	0.3147	0.2084	57.10	57.13
III	H	Br	" " bromide	123.5-124.5	90	0.3215	0.2190	57.12	—
						0.2924	0.1722	50.78	50.70
IV	H	I	" " iodide	102-102.5	85	0.3005	0.1772	50.84	—
						0.2514	0.1722	45.37	45.32
V	H	CN	" " cyanide*	95.5-96	96	0.2613	0.1336	45.70	—
						0.2465	0.1677	58.66	58.72
VI	H	CNS	" " thiocyanate	73-73.5	93	0.2543	0.1731	58.69	—
						0.3244	0.2067	53.70	53.68
VII	CH ₃	OCOCH ₃	3-Methoxyalkyl mercuric acetate	31.5-32	71	0.3152	0.1956	53.51	—
						0.3103	0.1844	51.24	51.62
VIII	CH ₃	Cl	" " chloride	103-103.5	90	0.3032	0.1803	51.44	—
						0.3310	0.2098	54.65	54.94
IX	CH ₃	Br	" " bromide	133-133.5	91	0.3143	0.1994	54.70	—
						0.3458	0.1956	48.77	48.97
X	CH ₃	I	" " iodide	147-147.5	85	0.3269	0.1844	48.63	—
						0.2844	0.1446	43.84	43.93
XI	CH ₃	CN	" " cyanide	53-54	90	0.2645	0.1341	43.71	—
						0.3005	0.1979	56.81	56.41
XII	CH ₃	CNS	" " thiocyanate	91-91.5	85	0.3140	0.2062	56.64	—
						0.3341	0.2010	51.90	51.74
XIII	C ₂ H ₅	OCOCH ₃	3-Ethoxyalkyl mercuric acetate	Oil	56	0.3298	0.1975	51.64	—
						0.2148	0.1241	49.81	49.82
XIV	C ₂ H ₅	Cl	" " chloride	58.5-59	75	0.2312	0.1330	49.60	—
						0.2403	0.1467	52.64	52.91
XV	C ₂ H ₅	Br	" " bromide	61-61.5	72	0.2269	0.1392	52.90	—
						0.2108	0.1160	47.45	47.35
XVI	C ₂ H ₅	I	" " iodide	66-66.5	70	0.2255	0.1239	47.37	—
						0.2351	0.1161	42.48	42.62
XVII	C ₂ H ₅	CN	" " cyanide	Oil	56	0.2041	0.1033	42.64	—
						0.3042	0.1921	54.45	54.27
XVIII	C ₂ H ₅	CNS	" " thiocyanate	80.5-81	82	0.3101	0.1953	54.35	—
						0.3207	0.1848	49.70	49.94
XIX	H		Di-(3-hydroxyalkyl)mercury	113-114	90	0.3210	0.1849	49.67	—
						0.2831	0.1533	46.70	46.58
XX	CH ₃		Di-(3-methoxyalkyl)mercury	59-59.5	85	0.2799	0.1510	46.52	—
						0.2948	0.1492	43.64	43.74
XXI	C ₂ H ₅		Di-(3-ethoxyalkyl)mercury**	52-52.5	82	0.2869	0.1457	43.80	—
						0.2801	0.1341	41.28	41.22
						0.2748	0.1321	41.44	—

* Found %: N 4.48, 4.38. Calculated %: N 4.10.

** Found %: C 44.63, 44.65; H 7.88, 8.02. Calculated %: C 44.38; H 7.80.

were recrystallized from petroleum ether or alcohol.

Symmetrization of 3-Hydroxy-, 3-Methoxy-, and 3-Ethoxy-2,2,3-trimethylbutyl Mercuric Acetates [3].

A solution prepared from 25 ml of a 40% sodium hydroxide solution and 10 g of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ in 5 ml of water was added with continuous efficient stirring to a solution of the hydroxyalkyl mercuric acetate (I; 6 g) or to an emulsion of the methoxy alkyl mercuric acetate (VII; 6.1 g) and the ethoxyalkyl mercuric acetate (XIII; 6.4 g) in water (60 ml). The mixture was stirred for one hour more; the dark precipitate was filtered, washed with water, and extracted with acetone. Water was added to the acetone solution until cloudiness appeared. The crystals which separated on cooling, were dried over calcium chloride and recrystallized from ethyl alcohol.

Di-(3-hydroxyalkyl)mercury (XIX), and the corresponding methoxy (XX), and ethoxy compounds (XXI) (alkyl = 2,2,3-trimethylbutyl) were readily soluble in acetone.

Comparison of the melting points of the γ -mercury alcohols and their methyl and ethyl ethers makes possible the following conclusions.

1. Each of the organo-mercury compounds obtained containing a methoxy group [3-methoxyalkyl mercuric salts and di-(3-methoxyalkyl)mercury] have a higher melting point than the corresponding compounds.
2. Of the organo-mercury compounds containing a hydroxy group, 3-hydroxyalkyl mercuric acetate, chloride, and cyanide, as well as di-(3-hydroxyalkyl)mercury, melt higher than the corresponding methoxy compounds, whereas the melting points of 3-hydroxy- and 3-methoxyalkyl mercuric bromides, iodides, and thiocyanates are characterized by the reverse relationship.
3. The fact must be especially mentioned that, whereas in the 3-methoxyalkyl mercuric series and the 3-ethoxyalkyl mercuric series the melting point of the salts increases in going from the acetate to the chloride, to the bromide, and then to the iodide, the iodide in the 3-hydroxyalkyl mercuric series does not follow this rule; the melting point of the iodide is lower than the temperature of the bromide of this organo-mercury compound.

SUMMARY

1. Cleavage of the three-membered ring occurs by the action of mercuric acetate in water or in alcohol (methyl and ethyl) on the cyclopropane hydrocarbon (1,1,2,2-tetramethylcyclopropane), 3-hydroxyalkyl mercuric acetate, and 3-methoxy- and 3-methoxyalkyl mercuric acetates, respectively are formed (alkyl = 2,2,3-trimethylbutyl).
2. 3-Hydroxy-, 3-methoxy-, and 3-ethoxy-2,2,3-trimethylbutyl mercuric chlorides, bromides, iodides, cyanides, and thiocyanates were obtained by the substitution reaction of the acetates with KCl , KBr , KI , KCN , and KCNS .
3. Symmetrization products, di-(3-hydroxyalkyl)mercury, di-(3-methoxyalkyl)mercury, and di-(3-ethoxyalkyl)mercury (alkyl = 2,2,3-trimethylbutyl) were obtained by the action of an alkaline solution of sodium stannite on 3-hydroxy-, 3-methoxy-, and 3-ethoxy-2,2,3-trimethylbutyl mercuric acetates.
4. Certain generalizations were established for the organo-mercury compounds synthesized on the change of the melting point in relation to the nature of the anion combined with the mercury, and the nature of the functional groups (OH , OCH_3 , OC_2H_5) bound to the γ -carbon atoms.
5. All of the synthesized organo mercury compounds (21 preparations), except (I) and (II) which were reported in the first communications, are first being reported.

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Received February 16, 1953

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awarded the Order of Lenin

